THE EFFECT OF ALLOY AND IMPURITY VARIATION ON THE TREATMENT, CASTING AND PHYSICAL PROPERTIES OF ALUMINIUM-SILICON EUTECTIC ALLOYS.

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ABSTRACT

The aluminium-silicon eutectic alloy finds widespread use in commercial light alloy foundries world-wide. The intrinsic characteristics which ensure that this traditional alloy continues in use are excellent fluidity, moderate strength, good ductility, low shrinkage, no requirement for post casting heat treatment and exceptional corrosion resistance. The latter two are particularly noteworthy as they assure the eutectic alloy finds favour in numerous roles for which the higher strength Al-7%Si-Mg alloy is less well suited.

The research reported in this thesis aimed to quantify the changes in physical and structural properties of sand-cast Al-Si eutectic alloy due to compositional variations within the specified range provided by British Standard 1490-LM6. The eutectic alloy was selected for investigation primarily due to members of the local (NZ) aluminium industry expressing concerns regarding consistent production of castings capable of surpassing the physical requirements of the BS1490-LM6 standard.

To achieve the desired aim approximately 500 standard test bars (as used in industry and specified by BS1490) were produced using conditions replicating those encountered in a small, commercial foundry. Each specimen cast was of varying composition with the major variables being Na, Sr, Ti, B, Si, Mg, Mn and Fe. Physical and structural properties including: hardness, tensile strength, ductility, 0.2% proof strength, porosity, grain size and eutectic silicon morphology were monitored for each specimen produced. The combined composition and physical/structural data were then subjected to extensive statistical analysis via multi-linear-regression. The results of the statistical analysis are presented as a series of expressions relating the measured properties to the relevant compositional variables. The sometimes complex and inter-related effects of the elements responsible for significant property variation are illustrated in both numerical and graphical forms.

The full analysis results and associated findings are too numerous to be summarised here. An example of a significant finding is that, with the exception of grain refinement, boron is detrimental to every property monitored. Almost without exception the unwanted effects

of boron are already manifest at boron levels as low as 0.01%. Another finding of interest is that within the confines of the given compositional range, the controversial practice of adding manganese to counteract iron-induced embrittlement has little effect on ductility while being highly deleterious to tensile strength. Indeed the embrittling effects of iron were found to be far smaller in magnitude than anticipated given the concern which surrounds this element. This led to the conclusion that further investigation into the effects of iron on parameters such as fatigue endurance warrant investigation.

Two compromises were unavoidable in this research firstly, an inability to assess the level and hence effects of phosphorus variations, and secondly the boron additive used was not of the desired type. Surprisingly, the effects of boron mentioned above were not found to be discernibly influenced by the latter compromise.

Two less significant areas of experimentation were also touched upon in the course of this research, namely the suitability of various materials for use in conditions requiring contact with molten aluminium, and the contamination and compositional variations which occur during degassing by conventional lance and tablet methods.

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CONTENTS

Points of Significance

a) Unless otherwise specified all of the compositions alluded to in this thesis are in units of weight percent.

b) The exact composition of the various cast specimens depicted in the photomicrographs throughout this thesis may be found in Appendix H.

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SYMBOLS, ABBREVIATIONS AND UNITS

A	Projected Area (m^3)
AA	Alumimum Association
AFS	American Foundrymen's Society
AFS#	AFS Modification Rating
"ALPUR"	A melt purifying method developed by Pechiney
ANN	Artificial Neural Network
ANOVA	ANalysis Of VArience
AS	Australian Standard
ASTM	American Society for Testing and Materials
ASTM G(M)	ASTM Macro-Grainsize Rating
ASM	American Society for Metals
atm	Atomic
BS	British Standard
BSPT	British Standard Pipe Taper (Thread)
cc	Cubic-Centimetre
^oC	Degrees Celsius
C_w	Drag Coefficient
DAS	Dendrite Arm Spacing (μm)
Dia.	Diameter
g	Gram
g	Acelleration due to Graverty = $9.81 m/s^2$ (Appendix C only)
h	Hour
h	Hydrostatic pressure (Pa)
HIP	Hot Isostatic Pressing
Hv	Vickers Hardness (kg/mm^2)
I.D.	Inner-Diameter
IPENZ	The Institution of Professional Engineers (NZ) Incorporated
J	Joule
KBM	Kawecki Billiton Metaalindustrie
kg	Kilogram

ℓ	Litre
LPG	Liquefied Petroleum Gas
m	Metre
M	Mega = 1×10^6
min.	Minute
"MINT"	Melt IN-line Treatment (a process developed by Consolidated Aluminium)
ml	Millilitre = Litre/1000
MLR	Multi-Linear-Regression
mm	Millimetre = Metre/1000
NZ	New Zealand
NZAS	New Zealand Aluminium Smelters Limited
O.D.	Outer-Diameter
OES	Optical Emission Spectroscopy
P	Pressure (Pa)
Pa	Pascal
PC	Personal Computer (IBM or clone)
PPI	Pores Per Inch
ppm	Parts Per Million
PS	Proof Strength (0.2%) (MPa)
Q	Quality Index (MPa)
r	Radius (m)
Ref.	Reference
RM	ReMelt
RPT	Reduced Pressure Test
s	Second
sec.	Second
Std	Standard
STP	Standard Temperature and Pressure
t	Time (sec.)
TPRE	Twin-Plane-Re-entrant-Edge
TS	Tensile Strength (MPa)

V	Volume (m^3)
wt	Weight
XRD	X-Ray Diffraction
α	Alpha = Statistical error margin
δL	Delta L=Change in length
ν	Nu = Velocity (m/s^2)
μ	Mu (Mju)=micro=1×10^{-6}
π	Pi = 3.14159
ρ	Rho = Density kg/m^3
3D	Three Dimensional
"	Inch

R^2 and other statistical factors are defined in section 7.2

1.0 INTRODUCTION

Following the development of the Hall-Heroult process in 1886, the four major issues which have enabled aluminium to become a major industrial metal are: Wilm's discovery of age hardening, Pacz's discovery of silicon modification, the Second World War and the realisation that the world's oil reserves are limited. Wilm's and Pacz's discoveries are the main metallurgical advances which have enabled the development of the vast majority of cast and wrought alloys in use today; Pacz's discovery in particular, is covered in some detail later in this report.

The Second World War caused demand for light alloys to soar as aircraft designers employed lighter and stronger materials to reduce the weight and improve the performance of military aircraft then being manufactured by the thousand. During this period, acceptance and technical knowledge regarding light alloy processing and properties improved immensely. The huge increase in demand for aluminium resulted in upscaling of the aluminium industry and large reductions in production costs mainly due to improved economies of scale. Reduced metal costs and more widespread familiarity allowed aluminium to become a viable alternative material for the production of countless artefacts, an issue which was vigorously pursued by aluminium producers as aircraft production slowed with the end of hostilities.

Since the fuel crisis of the early seventies, energy efficiency has assumed ever more importance thus transport sector manufacturers have increasingly turned to aluminium alloys to reduce vehicle weights so improving performance and economy. Since the '70s European and Japanese manufacturers have converted almost exclusively to cast aluminium cylinder heads, blocks, transmission housings and wheels -all items which have traditionally been cast in iron or pressed from steel. The increased use of aluminium by these manufacturers has culminated in Audi recently introducing a semi-mass-produced automobile featuring extensive use of aluminium in the mechanical components listed above as well as having a floorpan/chassis and body panels manufactured exclusively from aluminium alloys. North American manufacturers have also rapidly increased their use of light alloy components, particularly castings. However the scope for further expansion in

this market is still large. This worldwide increase in the use of cast aluminium has driven the development of alloys and processing steps which have resulted in higher quality products at lower cost.

The North American commercial aircraft industry has been cited[1] as an example of how important it is to stay abreast of developments in cast aluminium alloy processing. In the 1980s, US Aircraft manufacturers accounted for 95% of the world's market for commercial jets; in 1995 the figure is 65-75%. One of the main reasons given for the increased market penetration by European manufacturers (such as Airbus) has been a lack of acceptance by North American authorities of the huge advances made in cast component quality and integrity. An illustration of this is that Boeing and MacDonnell Douglas are restricted to the use of forged "hogouts"* while Airbus uses similar cast items. On a four engine aircraft such as the Airbus A340 this equates to a saving of approximately $100,000 US per aircraft.

A direct result of the improved knowledge, integrity and use of aluminium castings has been that worldwide, ever more designers specify cast aluminium as the material of choice for articles ranging from one-off minor components to mass produced critical and intricate structural members.

Light alloy founders are today faced with the challenge of continually striving to maximise the quality and consistency of their products without compromising cost so as to retain their positions in an expanding but ever more demanding and competitive market. This remark holds true globally from large foundries supplying mass-market products to huge corporations through to the smallest foundries supplying one-off components to a local market.

Al-Si Alloys

Almost all commercial aluminium foundry alloys contain substantial quantities of silicon. This addition is used to reduce casting temperatures, improve melt fluidity and decrease shrinkage and thus improve mould filling and casting reliability. Due to excellent

* Wing engine attachment frames.

castability, alloys of this type can often produce mechanical properties in difficult to fill regions which are superior to those obtainable with less-castable, higher-strength alloys. Possibly the single most common group of casting alloys within the Al-Si range are the Al-7%Si-Mg alloys such as B.S.1490-LM25 (AA356, AA357, AS601, etc), hence these alloys have been the subject of intense study for several years. The processing steps carried out during the production of castings from this alloy are common to almost all hypoeutectic Al-Si alloys. By virtue of this, the mass of information available on Al-7%Si-Mg alloys has greatly influenced and assisted improvements in the understanding of alloys such as the Al-Si eutectic alloy B.S.1490-LM6 (AA413, AS401, etc). The eutectic alloy is of particular relevance as it has a low solidification temperature and an extremely narrow temperature band over which solidification takes place (see Figure 1).

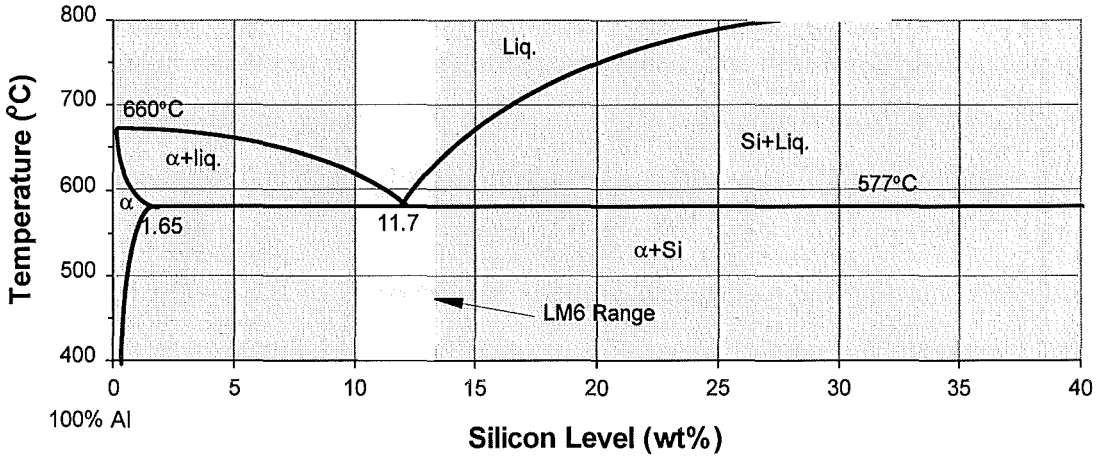


Figure 1: The aluminium-silicon phase diagram.

In several common situations the aluminium-silicon eutectic (LM6) alloy has some important advantages over Al-7%Si-Mg (LM25), the main points being increased fluidity and reduced shrinkage, greater corrosion resistance, good wear resistance and no need for post-casting heat-treatment. For these reasons, when marine or large components are required, LM6 is often selected as the alloy of choice. LM6 also lends itself to use in small foundries where simplicity of mould design and lack of subsequent heat treatment may be production necessities.

Foundries in New Zealand have traditionally specified LM6 for a myriad of applications primarily due to familiarity and the comparative ease associated with the casting of this alloy: given the small scale of New Zealand foundries, the use of LM6 is also often due to

necessity. The most significant composition limits imposed by British Standard 1490[(2)]-LM6 are shown below (a more complete description may be found in Appendix A):

	(wt%)
Si	10-13%
Fe	0 - 0.6%
Mn	0 - 0.5%
Mg	0 - 0.1%
Zn	0 - 0.1%
Cu	0 - 0.1%
Sn	0 - 0.05%
Ti	0 - 0.2%

The appreciable levels of iron and manganese permitted allows secondary metal producers to provide LM6 with substantial levels of impurities. This results in the legitimate sale of LM6 alloy with widely differing compositions from batch to batch and supplier to supplier.

Unfortunately, meeting the mechanical property requirements of B.S.1490-LM6 not only requires consistent and controlled casting practice but close control over variations in composition of the melting stock used. The usual casting process followed with both the LM25 and LM6 alloys may be summarised as:

Melting
↓
Degassing
↓
Modification
↓
Grain Refinement
↓
Casting.

The success of the three critical intermediate steps is dependent upon prior knowledge and control over the *exact* alloy composition hence minor compositional variations between one melt and the next can result in widely differing physical and structural properties. A consequence of this largely inherent composition-induced variability is that several foundries have experienced great difficulty optimising their processing procedures to

achieve consistent cast properties. The implementation of tight controls regarding the source of incoming ingot and the rate of in-house returns entering each melt has gone some way to resolving these problems.

Using conventional commercial casting practices, it is widely felt* that only very specific alloys within the LM6 range may be capable of producing mechanical properties in accordance with the specified requirements. With optimal modification, grain refinement and the use of "corrective" procedures, such as the addition of Mn to high Fe alloys it is still doubtful that all alloys within the LM6 range may ever meet the physical standards required. Very little quantified data exists regarding the effects of impurities commonly present within LM6 alloy hence confirming the above statements is difficult.

This research set out to resolve some of the uncertainty surrounding the effects of composition variation on the properties of alloys within the BS1490-LM6 range. The aim of this research was to quantify the effects of as many composition variations as possible, so providing a true gauge of the influence of the most significant alloying elements and impurities and their interactions. Attempts to find prior experimental data to definitively resolve the most significant issues were largely fruitless and hence no alternative existed other than to produce and analyse numerous alloys spanning the composition range of interest. The initial compositional variables, along with the ranges in which they were to be produced, are listed below.

	(wt%)
Silicon	10-13%
Iron	0 - 0.6%
Magnesium	0 - 0.1%
Manganese	0 - 0.5%
Strontium	0 - 0.05%
Sodium	0 - 0.05%
Phosphorus	≈ 4 - 11 ppm

While not specified in the relevant standards, phosphorus was included as an investigation variable as it was felt that this element could account for some of the unexplained

* D. Irwin, NZAS, Personal Correspondence

variability in properties encountered by local foundries. The successful inclusion of phosphorus as an experimental variable relied on the ability of New Zealand Aluminium Smelters Limited (NZAS) to chemically analyse specimens to a level of ± 1 ppm Phosphorus. Unfortunately, even after extensive efforts in this area, accuracies no greater than ±4 ppm could be obtained so forcing this experimental variable to be dropped as the main focus of investigation. Subsequent to the exclusion of phosphorus, both titanium and boron were added to the main investigation list yielding the final range of composition variables listed below. The physical and structural properties monitored for each final cast alloy produced are also listed.

Final Aim Composition Ranges		*Physical Properties Monitored*
Silicon	10-13%	
Iron	0-0.6%	Tensile Strength
Magnesium	0-0.1%	0.2% Proof Strength
Manganese	0-0.5%	Ductility
Sodium	0-0.05%	Grain Size
Strontium	0-0.05%	Porosity
Titanium	0-0.2%	Hardness
Boron	0-0.05%	Modification Level

Large numbers of cast specimens of varying composition were required to successfully investigate the above parameters, as the variability associated with each of the measured properties was unknown. Therefore full advantage could not be taken of classical experimental design procedures.

To simplify sample production and to optimise the relevance of the final results to local industry, the final cast samples were produced by techniques and in an environment similar to those encountered in a small commercial foundry. Efforts to replicate commercial foundry practices necessitated initial investigation into the contamination of melts by various degassing lance materials and the influence of various degassing methods on melt composition. The final cast specimens from which the bulk of this investigation draws consisted of sand cast test bars as laid out in BS1490 and standard composition disks as described in ASTM E716[3].

Extensive mechanical testing and quantitative structural analysis of the final cast specimens resulted in the collection of some 17,000 plus observations relating to the cast properties and compositional variables. These thousands of recorded observations were then analysed by computerised statistical analysis (multi-linear-regression). Multi-linear-regression (MLR) allowed discrimination and quantification of the various effects each composition variable had upon the monitored structural and physical properties. Interactions between the impurity elements were subject to indepth investigation, especially when: compounds of the elements in question were known to exist; interactions had been indicated by commercial practices or reports by previous authors suggested possible interactions of significance. The final results of this analysis consisted of a series of statistically irrefutable equations, relating the significant compositional variables to the measured cast properties. Given an exact or anticipated final casting composition the MLR-derived equations provide a basis for forecasting these resulting cast properties. The final expressions not only quantified the effects of the major chemical variations but also revealed the effects of a number of very important interactions which have previously been unknown or the subject of confusion and controversy.

It is hoped that the highly significant quantified results are of a form which is directly applicable and informative to people in situations ranging from the foundry floor to academic institutions.

2.0 LM6 BACKGROUND THEORY: A Literature Review

2.1 EUTECTIC SOLIDIFICATION

The range of compositions permissible within the BS1490-LM6 standard allows the formation of hypo-, hyper- or fully eutectic structures. The composition relating to the actual eutectic point is still open to some question, however it is generally accepted as being 11.7%Si in pure Al-Si alloy[6] (see Fig. 1). The impurities commonly encountered in commercial alloys move the eutectic to higher silicon values: this effect is promoted by faster-than-equilibrium cooling as is encountered in conventional alloy processing. The addition of modifying elements has possibly the single greatest effect on the eutectic position. Foseco[4] reports that when full modification is carried out the eutectic is shifted by as much as 1.3% to 13%Si while Abbott and Parker[5] report that with the use of modification and "suitable casting conditions" fully eutectic structures can be encountered with silicon levels as high as 15%. A consequence of this variability in the actual eutectic composition is that alloys within the LM6 range may constitute: over 25% primary aluminium with the remainder being eutectic, a fully eutectic structure or up to 2% primary silicon in a eutectic matrix. These structures are vastly different in their macro and microstructural appearance. However in each case, the vast majority of the structure is purely eutectic. To further complicate matters, modification (which is covered in the following section) does not occur uniformly. Hence variations in the cast structure from hypo- to hypereutectic forms may be found within a single casting[6].

In the unmodified state, when the Al-Si eutectic solidifies, the silicon phase leads the solid/liquid interface solidifying in a faceted manner. Major and Rutter[7] demonstrated this and noted that the solidifying face of the aluminium phase is concave in nature. This negative curvature is brought about by a build-up of silicon ahead of the solidifying interface as silicon is rejected by the solid aluminium-rich α-phase. As the faceted silicon leads the aluminium it is the silicon which controls the final microstructural morphology of the eutectic phase. In the presence of modifying elements, the silicon most likely grows by

the Twin Plane Re-entrant Edge (TPRE) mechanism, as suggested by Hellawell[8] and supported by the results and theories of Major and Rutter[7]. Kobayashi et al[9] carried out electron diffraction analysis of thin Al-Si films to study the crystallographic characteristics of individual crystals comprising of the typical eutectic microstructure. This study reaffirmed the preferential silicon growth direction as <112> with the habit plane of {111},thus supporting the theory of TPRE growth. It also confirmed that multiple twins run parallel to the direction of crystal growth. When heat flow in the growth direction or chemical disruption occurs these twins provide new twin habit faces allowing branching to occur while retaining the <112> growth direction. This is shown in Figure 2.

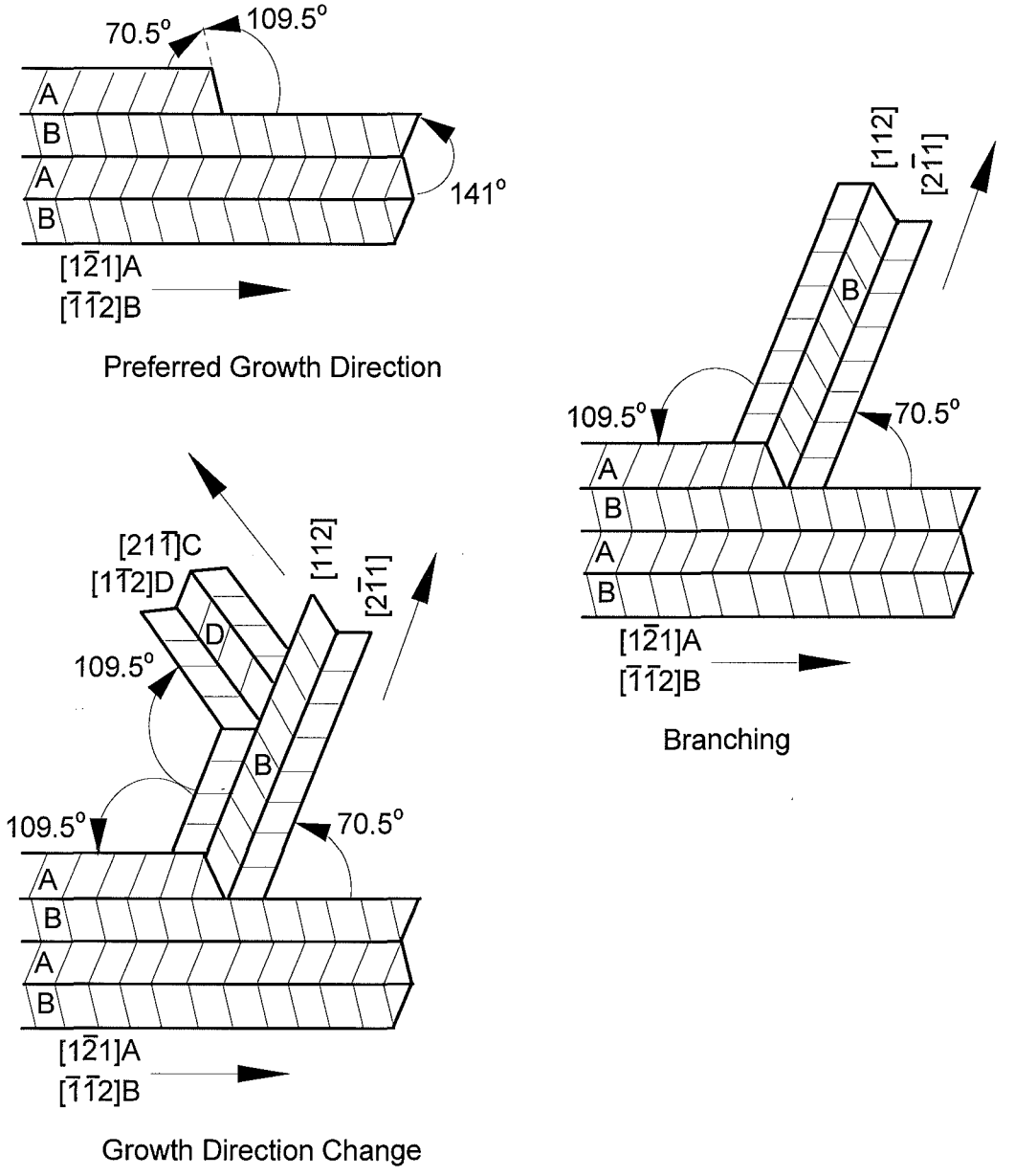


Figure 2 : Modification induced twin branching.

Kobayashi et al[9] also established that the eutectic aluminium grains have diameters comparable to the spacing between the silicon plates, indicating repeated aluminium nucleation upon the silicon phase. The apparently random crystallographic orientation relationships between the eutectic silicon and adjoining aluminium crystals were measured by selected area electron diffraction analysis and classified into relationships taking the growth habits and twin directions into consideration. It was found that 52% of the grains displayed the following relationship:

$$[001]\ Al \parallel [110]\ Si,\ [100]\ Al \parallel [\bar{1}1\bar{1}]\ Si.$$

Ohno et al[10] examined the microstructure of several eutectic systems so as to determine the origin of eutectic grains. Their results provide very clear indications as to what can be expected following the solidification of either hypo- or hypereutectic systems. Figure 3 schematically illustrates the two formation mechanisms suggested by these authors. When primary crystals of the eutectic's secondary phase (in this case Al)* are present, the eutectic does not nucleate from the primary crystal; rather the eutectic forms as independent columnar grains. If however the leading phase (Si) forms as a primary crystal (i.e. Al-Si hypereutectic alloys), equiaxed eutectic grains nucleate and grow from the primary phase, leading to a series of equiaxed eutectic colonies. The majority of the samples examined in this research were modified and, as a result, even the high silicon samples (≥13% Si) tended to show distinctly hypoeutectic structures. Typically, the high silicon samples showed structures of a form illustrated in Plate 1, i.e. a core of equiaxed primary aluminium dendrites surrounded by purely eutectic columnar grains. Plate 2 illustrates a sample of 13.7% Si which is made up of virtually 100% columnar eutectic grains. This very high silicon sample is only partially modified, yet shows no region of equiaxed eutectic indicating an absence of primary silicon crystals. Plate 3 shows a sample of virtually identical composition to Plate 2, with marginally less modifier. Although equiaxed eutectic grains are visible in Plate 3 so are primary aluminium dendrites, which highlights the heterogeneous nature of this type of alloy.

* The "aluminium" phase is actually an Al-Si solid-solution (termed α) which contains 1.65%Si as shown in Figure 1.

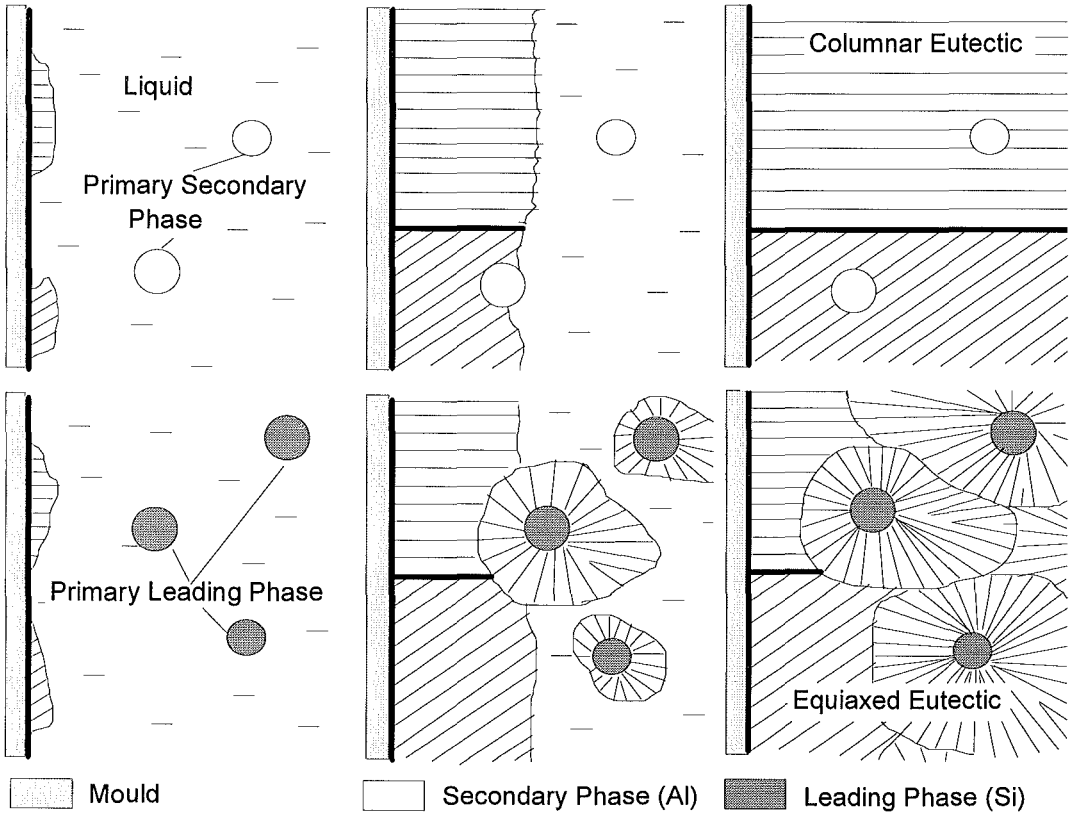


Figure 3 : Columnar and equiaxed eutectic growth.

As Abbott and Parker[5] note, when appreciable levels of impurity are present, the eutectic solidifies in a dendritic manner, i.e. as if it were a single primary phase with the liquid enriched in the impurity elements. Eventually, this solidifies as the ternary/quaternary eutectic between the eutectic colonies.

Plate 4 illustrates the same sample as Plate 2 with the ternary/quaternary regions highlighted. The central region of this sample contains an exceedingly fine colony region , a phenomena which may be due to the formation of skeletal silicon ahead of the colony solidification front. This method of solidification is diagrammatically shown in Figure 4 and relies on initial solidification of eutectic colonies in the undercooled outer regions of a hyper-eutectic casting (from Abbott and Parker[5]). The colonies continue to advance until the eutectic temperature is encountered, whereupon the hyper-eutectic silicon concentration allows continued growth of silicon ahead of the colony formation. The large silicon formations which result both inhibit the growth of eutectic grains and produce nucleating sites for new colonies resulting in regions of very fine grain (colony) size. Since skeletal

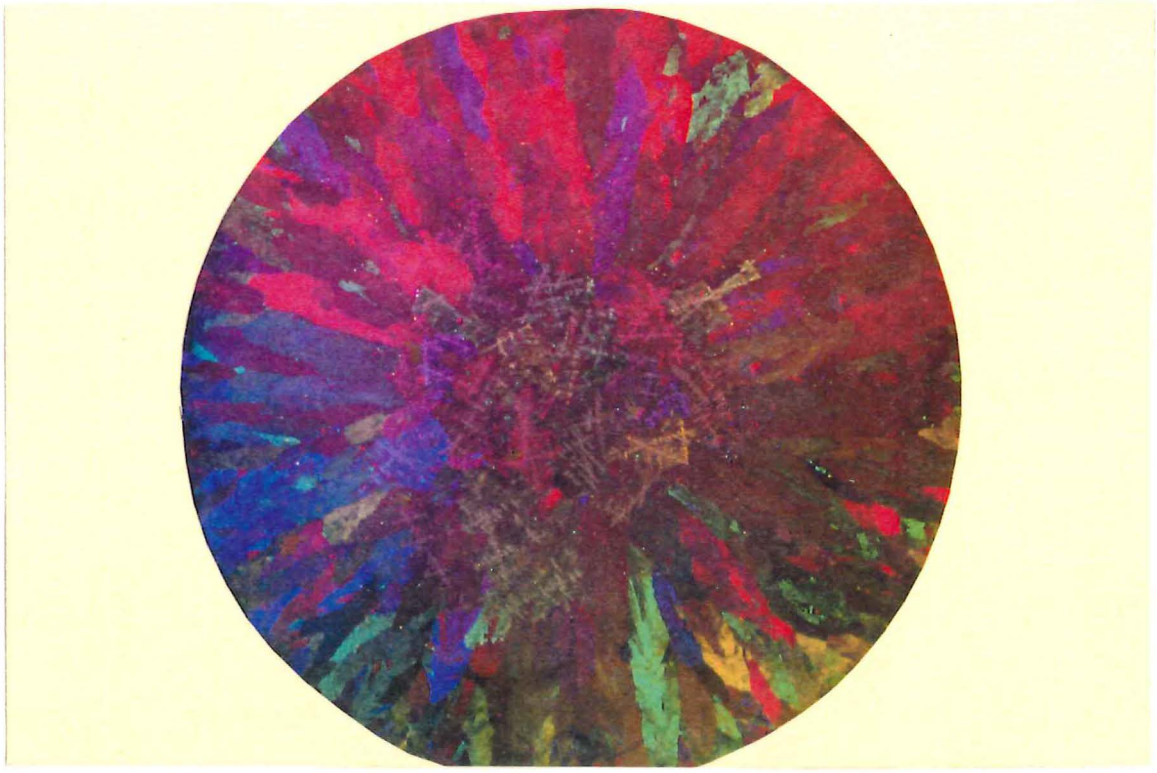


Plate 1: A high silicon (13%) cast structure displaying an equiaxed dendritic core with a columnar shell, sample 123-2-87 (x4.5).

Plate 2: A 100% columnar eutectic structure (13.7%Si), sample 83-3-26 (x4.5).

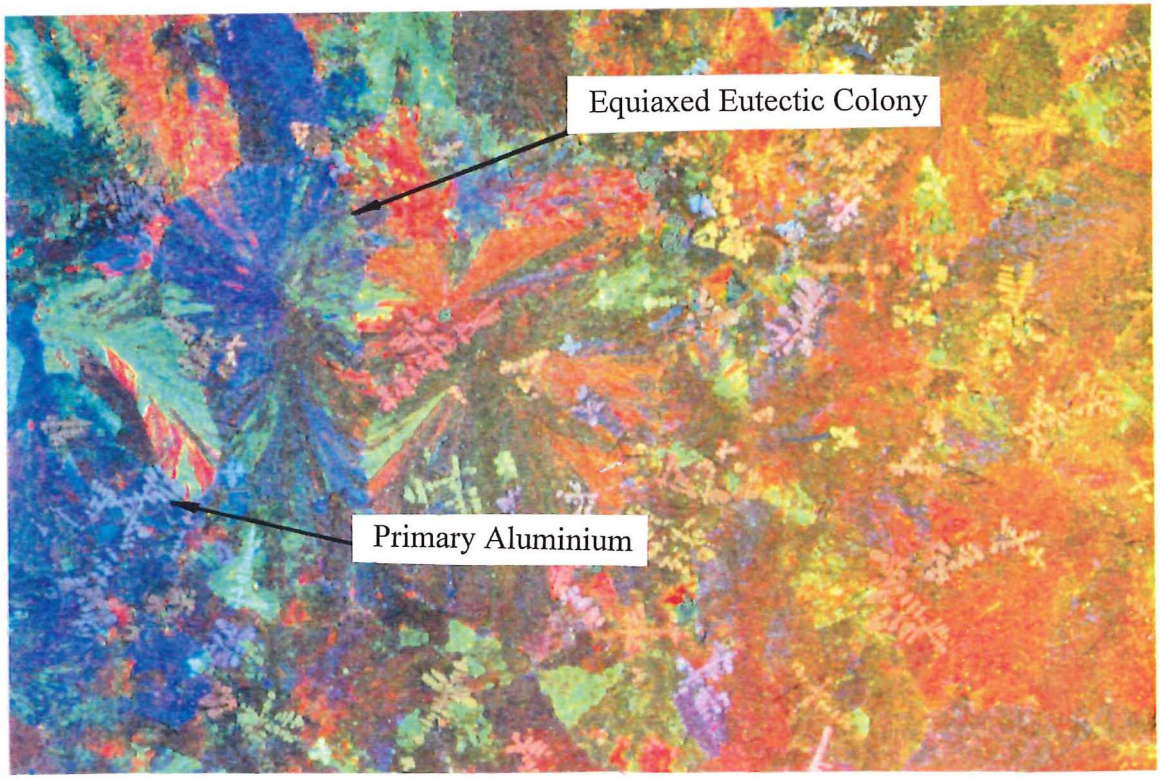


Plate 3: A eutectic structure displaying both equiaxed eutectic colonies, which have nucleated on primary silicon, and primary aluminium dendrites, sample 93-2-80 (x11.5).

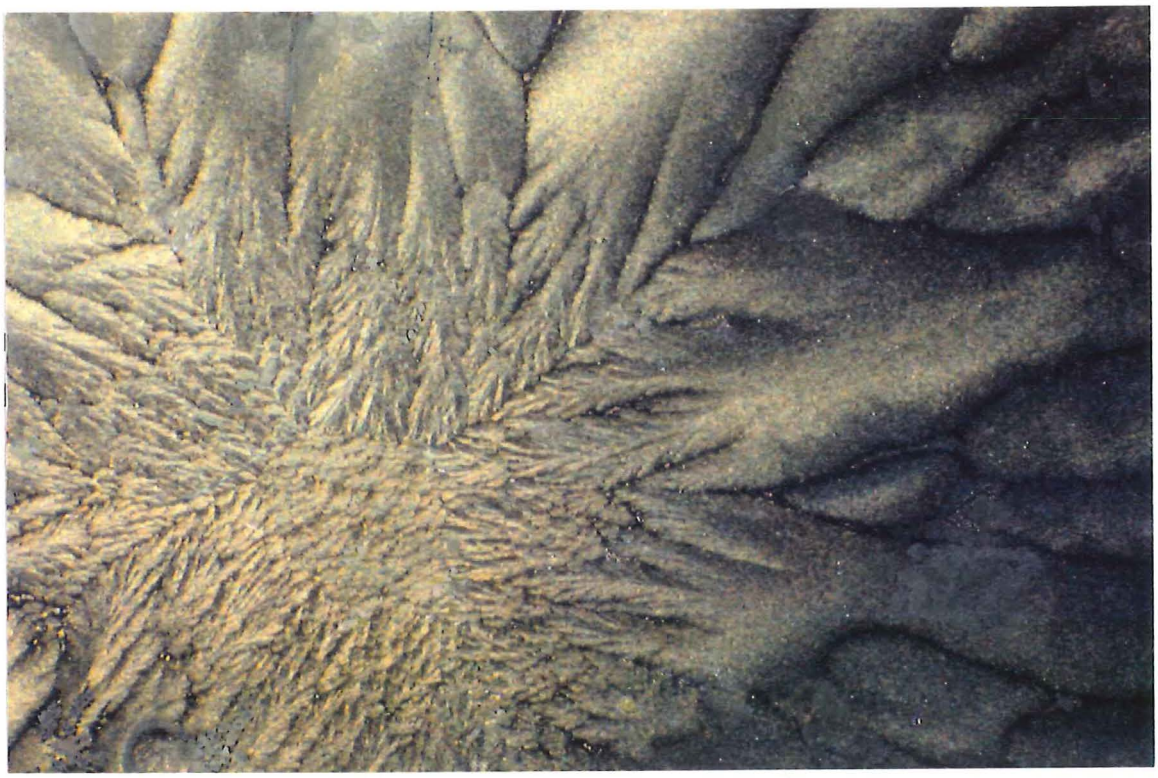
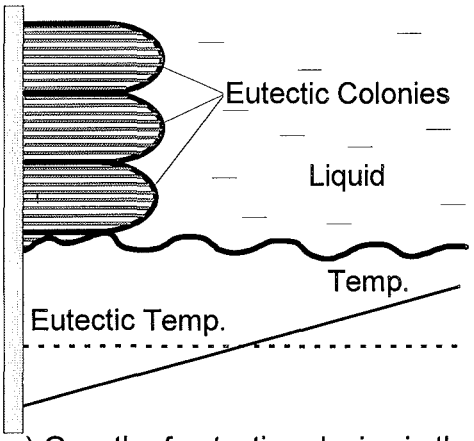
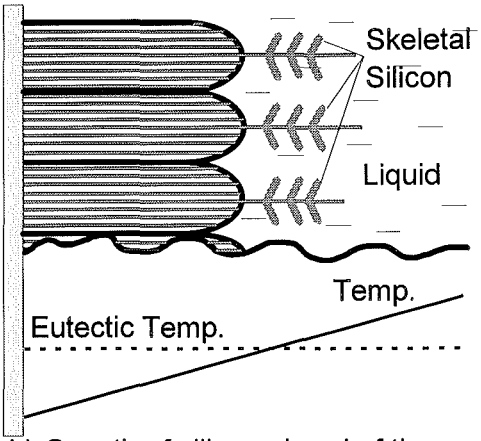


Plate 4: The central region of the sample displayed in Plate 2. Most probably refined by the presence of skeletal silicon (x11.7).

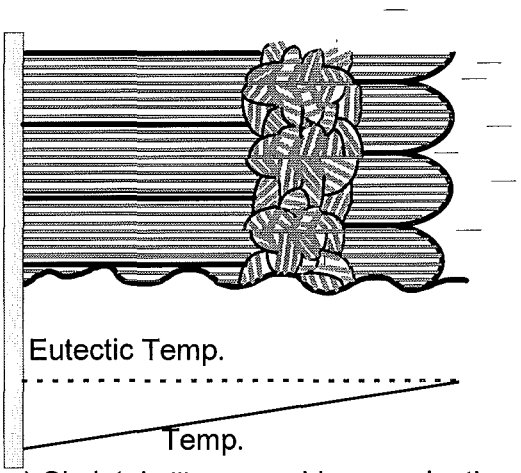
silicon was not observed in the microstructure of the sample illustrated in Plate 4 it was impossible to confirm the occurrence of this refinement mechanism. The only alternative explanation for the colony refinement illustrated in Plate 4 is that magnesium containing ternary phase, as observed in the boundary regions, collects ahead of the colony solidification front stabilising any recession which may occur. This divides the colony by repeatedly splitting the growth front. Reference to this latter mechanism has not been found and it is thought to have less merit than the former skeletal silicon scenario.



a) Growth of eutectic colonies in the undercooled region.



b) Growth of silicon ahead of the eutectic. Above eutectic temp. below liquidus temp.



c) Skeletal silicon provides nuecleating sites, and depletes silicon causing a return to a common growth interface.

Figure 4 : The formation of skeletal silicon and associate fine grained regions.

2.2 MODIFICATION

2.2.1 Modification Mechanisms

Modification involves a change in eutectic silicon morphology from coarse plates to fine interconnected fibres. This transition from what is termed an acicular structure to a fibrous one is accompanied by large increases in ductility, strength and machinability. Modification is possibly the single most important processing step in the production of Al-Si foundry alloys.

Modification was first observed by Frilley[11] in 1911 and later patented by Pacz[12] (1921), who produced refined eutectic silicon by the addition of alkali-fluoride salts to Al-Si alloys prior to casting. Since Pacz's patent, numerous studies and literature reviews regarding modification have been published thus a review of only the more interesting and recent publications will be covered here. Sigworth[13] produced an excellent review in 1983 which lists 50 relevant articles, almost all of which are easily obtained.

In the last 20 years the understanding of the modification process has greatly improved, yet even now there is not a perfect explanation of all the aspects surrounding silicon refinement. It is widely accepted that modification involves the adsorption of an impurity element onto the silicon phase during solidification. This prevents further growth upon the original TPRE and causes the formation of new twins, allowing variations in the direction of crystal growth (discussed below). This remains a disputed issue as papers are still being produced which question some of the most fundamental experimental results upon which current modification theory is based.

The common theory regarding chemical modification is that "modifier" elements adsorb onto the growth steps at the silicon solid-liquid interface. This prevents further growth along the [112] direction, in effect poisoning this growth direction. As shown earlier in Figure 2, silicon growth steps stem from twin boundaries with planes of silicon atoms stacking at 70.5° to the growth direction. If the modifying element has the correct atomic diameter it will induce the formation of a new twin and hence new silicon growth sites, allowing growth along directions other than the original [112] direction. This will only take place if the modifying elements adsorb and promote twinning by displacing a {111}

silicon layer growth step to the alternate stacking sequence. Using a simple hard sphere model, Lu and Hellawell[14] found that the optimal size ratio would be:

dia. modifier : dia. silicon = 1.646 : 1.

They then assessed the importance and feasibility of the impurity-induced twinning theory by comparing the ideal size criterion to the effects of several actual elements. It was found that based on size alone Ba, Sr, Eu, Ca, Yb, La, Na and Ce (largest → smallest) should all act as modifying elements with the optimum size falling between Yb and La. An ability to obtain reasonable levels of these elements in the molten alloy must also be considered hence factors such as melting point, vapour pressure and oxide formation are also of importance.

Lu and Hellawell's results agree well with the theory of impurity-induced twinning and indicate that strontium, barium, ytterbium and calcium should exert similar but weaker effects than sodium in modification and twin formation.

One source of debate which has been resolved is that chemical modification is accompanied by multiple twin formation. Past authors[15] have put forward experimental evidence suggesting that this is not the case, resulting in later theories by Flood and Hunt[16] supporting the possibility that modification is not due to impurity-induced twinning but rather a transition from faceted growth to non-faceted growth caused by increased solidification velocity and increased undercooling. The transition was thought to be brought about by changes in the solid interface kinetics as solidification growth rates increase. This theory was also thought to be supported by earlier work by Steen and Hellawell[17] indicating that fibrous silicon structures could be produced without the presence of sodium, provided the cooling rate was high enough. It has subsequently been shown[18A] that this is not the case as "modification" does not take place with rapid cooling; rather an exceedingly fine form of the unmodified eutectic is produced.

Another issue which has been questioned is depression of the eutectic arrest temperature as modification levels increase. Research at Aluminium Pechiney by Charbonnier[19] indicates very clearly that modification induces changes in the level of supercooling, the period of supercooling and the eutectic arrest temperature. Charbonnier's work is in total agreement with experimental work by Closset[20,21] at McGill University, Clapham[22] at Queens

University and Apelian[23] at Drexel University. The variations in these properties, as shown schematically in Figure 5, have in fact been the basis for production of commercial thermal analysis units specifically designed to assess the level of modification present (Pechiney's "Thermatest 2000" and Metallurgical Products and Technologies' "Alu Delta"). This seemingly indisputable experimental information was all available in 1984 yet authors such as Liu, Li and Liu[24] at the South China University of Technology, Guangzhou have disputed it as recently as 1991.

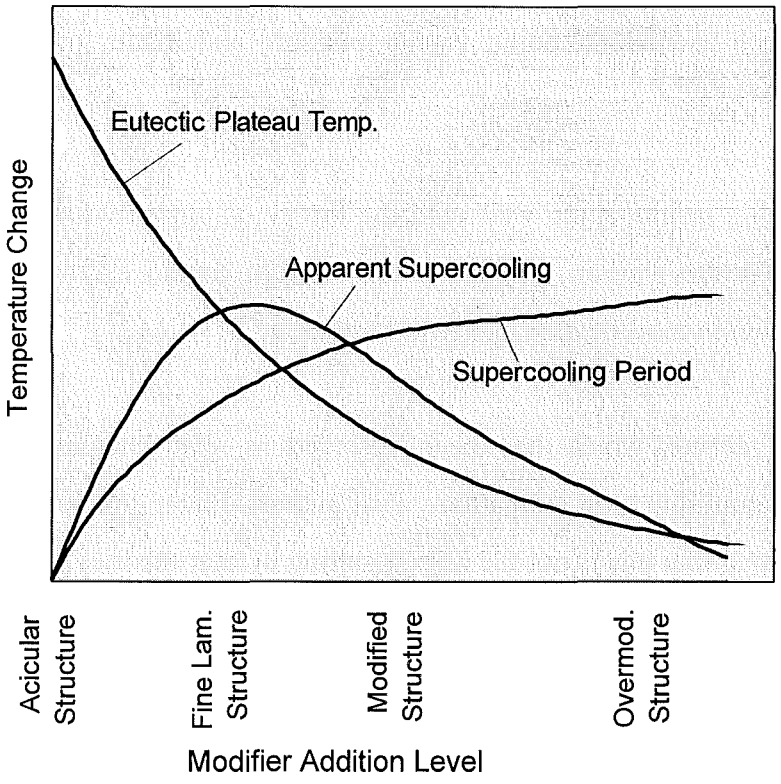


Figure 5: The thermal cooling effects of modification.

It should be realised that the definitions of the datum unmodified eutectic arrest temperature vary, hence the level of eutectic supercooling may vary depending on whether pure Al-Si alloy is used as the datum (577.3°C) or unmodified samples of the actual alloy being processed are used as "control" samples. If the former is used, thermal property variations may appear to be over four times larger than when the latter procedure is followed. The apparent variability in results may be the reason Liu et al questioned the occurrence of the eutectic depression. The other reason why results vary from one author to another is that the degree of undercooling caused by modification varies as the

solidification rate changes. Figure 6 which comes from data published by Glenister and Elliot[25] illustrates the significance that this often overlooked factor can have.

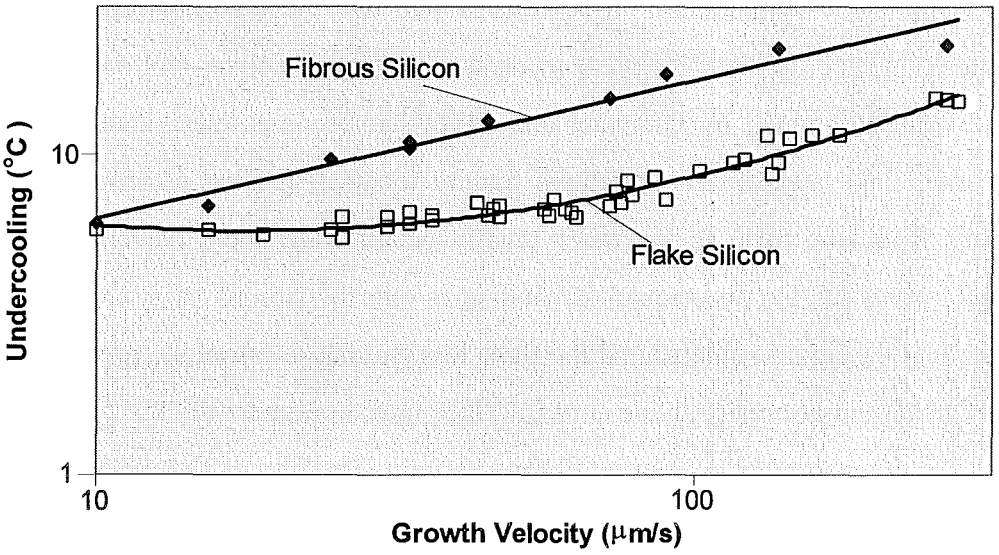


Figure 6: The effect of solidification rate on apparent eutectic undercooling (from Ref. 25)

Partial Modification

Clapham and Smith[19] carried out an extensive study into partially modified eutectic structures and as a result established guidelines as to the method of solidification apparent at the solid-liquid interface (and hence final morphology) for a range of solidification rates. At low growth rates (around 5 μm/s) mixed modification structures were observed until the modifier levels became so high (0.029% Sr) that a totally modified structure formed (as it did at all cooling rates). The mixed structure at these low growth rates was seen to consist of a modified matrix containing directional skeletal silicon as described in the preceding section (see Figure 4). Accumulation of modifier ahead of the main eutectic solidification front is thought to retard eutectic solidification and so promote continued skeletal silicon formation beyond the interface region. It would seem that skeletal silicon may form under two specific conditions: firstly for low growth rates with inadequate modifier and, secondly when the silicon level is slightly hypereutectic and rapid solidification initiates eutectic growth before the silicon level in the liquid has been depleted by the formation of primary silicon crystals.

When eutectic growth proceeded at the rate of 7-13 μm/s a distinctive banded structure was observed. This structure consisted of bands of modified and unmodified silicon transverse to the direction of solidification. It was found that at this critical growth rate each structure formed at the same temperature. It was also noted that the flake and fibrous structures were interconnected and had identical interphase spacings. When this data is compared with the results obtained by Glenister and Elliot[25] it becomes clear that at this critical growth rate, flake and fibrous structures require identical growth conditions and hence transitions from one form to the other readily occur. The most plausible explanation Clapham[22] gives for the occurrence of banding is that the fibrous structure absorbs more modifier than the liquid contains and the flake less, so that during flake growth significant levels of strontium are rejected ahead of interface into the liquid which sets up a modifier boundary layer, eventually promoting fibrous growth. The fibrous growth has the opposite effect depleting the modified levels in the boundary region, eventually causing reversion to the flake form.

At higher solidification rates, over 13 μm/s, the eutectic structure takes on the form of distinct unmodified colonies which are surrounded by modified regions. This structure results from the fibrous colonies rejecting modifier ahead of the advancing solid interface so allowing modified regions to form when the critical modifier level is reached. Since more undercooling is required to form the modified structure than the unmodified structure the modified regions recede from the solidification front and the fibrous colonies continue to control the final structural layout. The eventual structure which forms shows flake eutectic colonies surrounded by fibrous regions; this is the partially modified structure encountered in most castings.

Overmodification

Overmodification occurs in its clearest form when sodium modification is employed. When excessive sodium is used overmodification is evident as bands of aluminium within the eutectic which contain coarse silicon particles with distinctly non-faceted edges. Sigworth[13], Gruzleski[18] and numerous other authors attribute the overmodified structure to the accumulation of sodium ahead of the advancing solidification front. Eventually the sodium build-up yields Al-Si-Na compounds which nucleate large silicon crystals. The large silicon crystals cause rapid depletion of silicon in adjacent regions, resulting in

pseudo-primary aluminium forming around the silicon crystals. This process results in distinctive overmodification bands as are shown later in Plate 12, Section 6.1.

While several theories have been proposed to account for modification the most reasonable explanation is that modifying elements absorb onto the growth steps of the silicon liquid interface retarding the growth of this leading eutectic phase. The modifying elements change the {111} stacking sequence, so promoting "impurity induced twinning" which permits the silicon to branch and not be inhibited in its growth by relative crystallographic perfection. The aluminium then becomes the leading eutectic phase and dictates the final eutectic layout by solidifying in its non-faceted manner. This last point is supported by the observation by Lu and Hellawell[14] that modified eutectics contain columnar aluminium grains while unmodified eutectics consist of fine aluminium grains bounded by flake silicon plates.

2.2.2 Silicon Refiners and Refinement Effects

Sodium

The main commercial modifiers are sodium, strontium, antimony and, to a lesser extent, calcium. Sodium has the most pronounced and fastest acting refining effect of these elements but, due to its vapour pressure being very high (0.2 bar at foundry temperatures), it is very difficult to add in a consistent manner and fades rapidly once it has entered the melt. Due to this fading of sodium it is almost never added during foundry ingot production as its effects are usually lost in subsequent remelting and processing. Sodium is of particular importance with the eutectic alloy as it is capable of promoting finer structures than any of the alternative elements. Consequently the potential property improvements using sodium are far higher with the eutectic alloy than most other commercial alloys. As sodium must be added in the foundry shortly before casting, estimates of the degree of sodium retention, and hence modification level, are limited to very rapid techniques such as thermal analysis, as mentioned earlier. The production of sodium master alloys is not a viable prospect as sodium loss during production is high and retained sodium levels are seldom high enough to be of practical use. This method of sodium addition has previously been attempted[26] on an experimental basis but without useful levels of success.

Sodium is usually added as either pure metal or in combination with salts in a fluxing mixture. Addition of pure metallic sodium has some advantages over the use of salts, mainly that it is cheap and that application is easy. The efficiency of metal retention in the melt immediately following addition is typically less than 15-20%, but this is still 3-4 times the sodium pick-up experienced when salts are used. Due to sodium's high reactivity with any moisture in the air, it is generally added in the form of vacuum-packed aluminium canisters such as Foseco's "Navac" and "Napac" products. The canisters are usually plunged under the melt surface (at around 720-740°C) ten to fifteen minutes prior to casting. The intended sodium level is usually around 0.015%, however this varies depending on the exact alloy being cast and the amount of impurity it contains.

Sodium salt fluxing additives have the advantage of being easy to handle and store, however their use takes several minutes and requires relatively high melt temperatures, typically 760-800°C. The high temperatures necessarily promote increased absorption of hydrogen into the melt and ultimately lead to increased porosity. The addition of sodium to eutectic alloys is covered in several references, namely Gruzleski[18B] and Foseco Ltd[27A].

Strontium

Over the past 20 years strontium has found increased use as a modifier in aluminium-silicon casting alloys. While strontium cannot give as fine or as uniform a eutectic structure as sodium, it has a far lower vapour pressure (10^{-3} bar) at casting temperatures and hence fade is nowhere near as rapid. Thus the use of premodified ingot becomes a practical proposition. An indication of the comparatively recent development of strontium modification is shown by the fact that the Al-Sr phase diagram was only established with any certainty in 1986, when Closset et al[28] published a paper bringing together work by several authors as well as combining information from fresh experimental work. Strontium is often added in the form of a 10%Sr-90%Al master alloy which (when added as rod) can be effective after as little as one to two minutes and have a decay time of over eight hours (cf Sodium $\approx$ 45 minutes)[29]. Although it is not common, strontium can be added in other forms such as 10%Al-90%Sr or pure metal. These possibilities were researched in some detail by Closset & Gruzleski[30-32] in 1981. Strontium is often the modifier of choice when permanent mould casting is employed as the increased cooling rate reduces the refinement differences between sodium and strontium to negligible levels.

Antimony

Antimony has found widespread use in Europe and Japan. The main attraction of this modifier is that its action is permanent. As fading does not occur in antimony modified foundry ingots, modifier additions are not necessary when processing premodified primary ingot or secondary metal. Antimony is not compatible with either sodium or strontium and when it occurs in combination with either of these elements increased levels of the dominant modifier are required to achieve a fibrous structure. This is dealt with in some detail by Handiak et al[33] and also briefly by Bercovicci[34]. The most complete data on this issue found to date is contained in a text by Gruzleski and Closset[18C] which contains a chapter dedicated to modifier interactions. Antimony is almost always used in permanent mould casting, hence the major issue within the scope of this research is that it will eventually find its way into secondary metal processed within the New Zealand environment. The reason antimony is not normally used in sand cast alloys is that it is incapable of producing a fully fibrous eutectic and hence, in slow cooling situations, it produces properties substantially below those possible with sodium or even strontium.

Of the other elements able to promote modification only calcium has found any commercial use. Calcium, like antimony, does not give the same degree of refinement as strontium or sodium, but if permanent mould casting is employed the chilling effect in combination with partial modification results in well refined structures. Although certain commercial operations such as Chrysler's Etobicoke plant have produced literally millions of permanent mould components using calcium modification[35] it is highly unlikely that calcium will enter the New Zealand foundry cycle at any significant level in the near future.

One element reported to modify eutectic silicon, for which little information has been found, is sulphur. Bhatnagar et al[36] presented a paper in 1964 illustrating the ability of sulphur to refine both primary and eutectic silicon in hypereutectic alloys. As-cast unrefined hyper eutectic alloys consist of larger primary particles of silicon in a coarse acicular eutectic, a structure which is exceedingly brittle. The characteristics of sulphur seem similar to that of sodium in that retention upon addition is less than 15% and optimal addition levels occur with around 0.01% modifier. The effect of sulphur to refine both

primary and secondary silicon is unique and unverified. However Clegg[37] reported in 1986 that the use of sulphur and sodium together produced refined primary and modified eutectic hypereutectic structures. Clegg also indicated that modification does not significantly affect wear resistance, an important issue when these alloys are considered as hyper-eutectic alloys are often specifically used for components subject to high wear such as pistons and engine blocks.

Primary Silicon Refinement in Hypereutectic Alloys

In 1933 Pacz[38] patented the addition of phosphorus to hypereutectic alloys. Phosphorus provides numerous AlP particles, which serve as strong nucleation sites for the growth of silicon. The resulting microstructure contains greatly refined primary silicon with associated improvements in strength, ductility, fluidity and machinability[18]. Not surprisingly, deliberate phosphorus addition to these alloys has subsequently found widespread commercial acceptance. The action of phosphorus is incompatible with modifiers such as sodium and strontium and, as a result, the processes are not usually conducted together and refined primary and eutectic silicon are not usually found within the same microstructure. Conventional eutectic modification has been reported[39] to result in tensile properties superior to that achieved using phosphorus. Even so, additives other than phosphorus are seldom used on a commercial basis. The effects of phosphorus are covered more fully in Section 2.7.

Various methods have been utilised to promote both primary silicon refinement and eutectic silicon modification. An example is "double refinement"[18D] which involves initial overmodification followed by fading and conventional modification using sodium, strontium or combinations of the two. In 1989 Sun and Loper[40] proposed the use of 0.04%P + 0.17%Ti + 0.20%Na and gave examples of the successful use of this combination.

The Effects of Modification

The effect of modification on the mechanical properties has been the subject of much research, debate and controversy. Some of the controversy and confusion no doubt stems from the variability in silumins (Al-Si alloys) investigated. The vast majority of reported data surrounds the Al-7%Si-0.3-0.9%Mg alloy series, a group of alloys which are usually

used in a heat treated form. With this alloy authors such as Garat[41] report that modification has "no effect on yield strength and little effect on ultimate tensile strength", however it does "strongly affect elongation" (in a positive manner). These comments are supported by the data provided by several other authors including Jaquet[42], Das Gupta et al[43] and Gruzleski[18E].

In an effort to simplify the physical characteristics of the Al-7%Si-Mg alloys, Drouzy et al[44] devised a quantitative property measure termed a "quality index". The concept of a quality index is now widely accepted and has enabled the true beneficial effects of correct modification to be realised. The quality index is defined as:

$$Q(MPa) = TS(MPa) + (K).\log \text{elongation}(\%)$$

where K is chosen so that Q is independent of yield strength.

Far less information exists regarding the effects of modification on the eutectic range of alloys. Comments by Rauta[45] along with data provided by Foseco Ltd[44] and Thall and Chalmers[47] indicate that, within this range of alloys, correct modification is highly beneficial to tensile strength and ductility. Foseco report tensile strength increases as high as 70% along with up to five-fold increases in ductility. Whilst Thall and Chalmers indicate increases in strength close to 60% and ductility increasing up to 650%! Except for some informed comments by Gruzleski[18E] very little data exists regarding the effects modification has on properties such as fatigue resistance.

Finally, it should be noted that modification is not simply a function of the modifying element level: the response of any particular alloy is also dependent on the method and form of modifier addition as well as the period between addition and casting. For example, sodium will act almost immediately following addition whilst addition of strontium in a coarse form (e.g. ingot master alloy addition) may require up to 45 minutes to provide maximum silicon refinement.

2.3 GRAIN REFINEMENT

2.3.1 Grain Refinement Mechanisms

Grain refinement of aluminium alloys has taken place in a controlled manner since the 1930s. Traditional methods have involved the addition of titanium, either at levels over 0.15% or at lower rates if the additions are made close to the time of casting. Over the last 20 years master alloys containing aluminium, titanium and boron have replaced the use of simple Al-Ti products in almost all Al-Si casting. Studies into the use of elements other than Ti and B by various authors[48,49] have shown that V, Zr, Ni and Cr are all good aluminium nucleants however none have found commercial acceptance for the production of conventional castings.

Grain refinement can take place due to any one, or combination of, the following:

- Rapid cooling
- Denucleation
- Growth hindering additions
- Dynamic methods (dendrite fracture)
- Nucleation.

Mondolfo[49] published a paper in 1983 which cited 228 publications dealing with the above processes in non-ferrous alloys, the bulk of which centred around aluminium and its alloys. Since 1983 the issue of refining aluminium, particularly castings, has been the subject of numerous further studies, the results of which have provided volumes of information; but have not definitively answered several fundamental questions which will be addressed in the following sections.

- **Rapid Cooling**

  Rapid cooling is seldom used primarily as a method of grain refining aluminium castings. The rate of heat extraction is governed by the mould type which is most often governed by the number, size and complexity of the product required. Moulds providing high heat extraction rates are generally employed to improve productivity in the production of medium to high volume items however the associated metallurgical gains are significant. The microstructural improvements

include: grain refinement, eutectic refinement (not modification) and reductions in the dendrite arm spacing (DAS). Of these three factors, grain size is possibly the least significant with regard to associated improvements in physical properties. Gruzleski[18F] briefly discusses the effects of rapid or chill casting, relating the process to the structural changes it causes. Morales et al[50] investigated the effects of various mould geometries: the significant changes in structure these authors observed were attributed to varying rates of cooling and the number and form of asperities occurring on the mould wall which act as solidification nucleation sites.

- **Denucleation**

  The principle of denucleation is to either remove or impede what would otherwise be the initial grain nucleation sites. This is carried out so that solidification is delayed until conditions are encountered which enable a far more abundant nucleation mechanism to proceed. It is thought possible that boron will act in this manner if it is added to alloys containing titanium such that the Ti:B ratio becomes less than 2.22:1. Denucleation is used in the eutectic modification process to remove phosphide nuclei by the addition of neutralising elements such as sodium which prevent the nucleation of primary silicon on AlP precipitates. On a grain refinement level aluminium-silicon casting is not intentionally subjected to this method of dendrite multiplication.

- **Growth Hindering Additions**

  If elements act to impede dendrite growth while not hindering nucleation, they will promote a fine grain size. Similarly, if compounds form in the grain boundary regions of a casting that do not break down during subsequent heating or working, grain growth will be hindered and finer eventual grain structures will result. The Al-Si cast alloys, which consist of dendrites surrounded by eutectic, are not effected by the latter process as dendrite growth is minimal due to the eutectic boundary constraints, and working of these cast products is not performed on a commercial basis (LM6 - the subject of this study is neither heat treated nor worked). Elements which impede initial dendrite growth are not intentionally added to aluminium castings, however increasing levels of silicon or some modifiers may well be expected to promote this form of refinement.

- **Dynamic Methods**

  This issue is well covered in the paper by Mondolfo[49] mentioned earlier, and has been the subject of some previous work at the University of Canterbury[51]. Dynamic refinement relies on fracturing dendrites as they grow so providing nuclei for fresh dendrite growth. Most studies on this subject have concluded that in most industrial situations the expense and complication of providing agitation to the melt far outweighs any potential gains. Two processes which do make use of this form of refinement are: continuous casting, where electromagnetic fields have replaced moulds, and rheocasting. A variation of this process which has shown encouraging results is the application of mould coatings substances which effervesce harmless gas bubbles when subjected to the molten metal. These bubbles break up dendrites as they form on the mould wall. The advantages of this procedure are simplicity and low cost. Cupini et al[52] investigated the effects of hexachloroethane addition to mould coatings on the cast structure of commercially pure aluminium and their studies indicate that for optimum results this process requires alloys with short solidification ranges. This suggests that LM6 is a prime candidate for this form of refinement. The problems which no doubt limit this process are the removal of evolved gas from the mould and selection of a thermally effervescent compound which does not effect modification (hexachloroethane will not meet this criteria).

- **Nucleation**

  Addition of aluminium nucleants promotes finer grain sizes provided sufficient nuclei exist to increase the number of successful nucleation events. This method of grain refinement is by far the most common, although it covers more than just the addition of nucleating agents such as titanium and boron. Apart from the issue of overall heat extraction, mould geometry can play a major role in grain refinement. If a mould is extremely smooth, temperature variations along the mould wall will fluctuate, mainly as a function of local thermal mass. If, however, a rough surface is present, gas pockets among the surface imperfections can cause regions of high and low heat transfer. This was the main area of Morales et al's[50] study mentioned earlier. Results from this study show that if optimal roughness is achieved the local temperature variations along the mould wall can promote increased nucleation and castings which display finer grains, not only in the chill but also in what would

otherwise be predominantly columnar regions. It is hard to imagine these mould geometry considerations applying to sand moulds which have inherently low heat extraction rates and high surface roughness.

2.3.2 Titanium Nucleant Processes

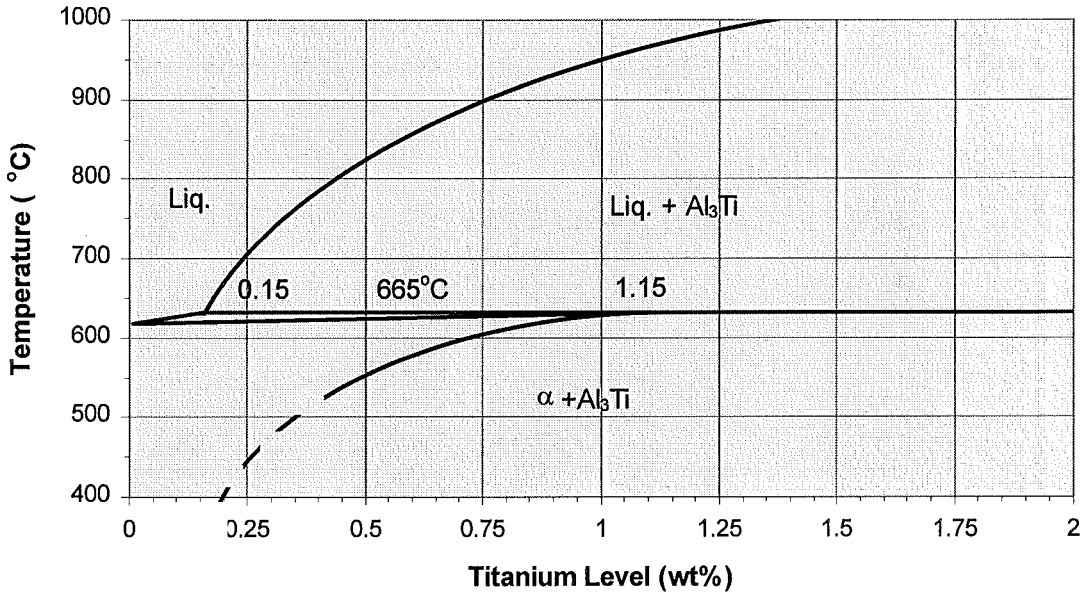


Figure 7: The aluminium-titanium phase diagram.

Traditional grain refining methods involve the addition of titanium to form Al_3Ti, which acts as an extremely potent nucleant for aluminium. As the Al-Ti phase diagram shows (Figure 7), titanium additions below 0.15% which are in the form of Al_3Ti dissolve and go into solution with aluminium. A result of this is that titanium additions below 0.15% are subject to quite rapid and pronounced grain refinement fade. In an attempt to avoid this problem several alloys, including BS1490-LM6, permit up to 0.2% Ti, however very few castings are produced at these high titanium levels. Most foundries add between 0.01-0.05% Ti which is sufficient to promote a fine grain size for approximately 30 minutes to one hour, depending on the addition form. Arnberg et al[53-56] have studied Al-Ti (and Al-Ti-B) grain refinement in some detail including the varying properties of the three most common Al_3Ti morphologies encountered. Some of the results of this research[56] are summarised in Figure 8. When Al_3Ti forms in a "blocky" structure it provides (011) planes to the melt which act as strong nucleating sites, hence the action of this form of aluminide is very potent. This structure is however, subject to rapid fade and is seldom

encountered after more than half an hour's exposure to the melt. Flake type Al_3Ti presents a (001) plane to the melt which does not provide as potent nucleation sites as the "block" structure. When "flake" type Al_3Ti is encountered complete dissolution and fade may take up to two hours to occur. The final form of titanium investigated was "secondary" aluminides which may form from the partial solution of boride containing Al_3Ti (see below).

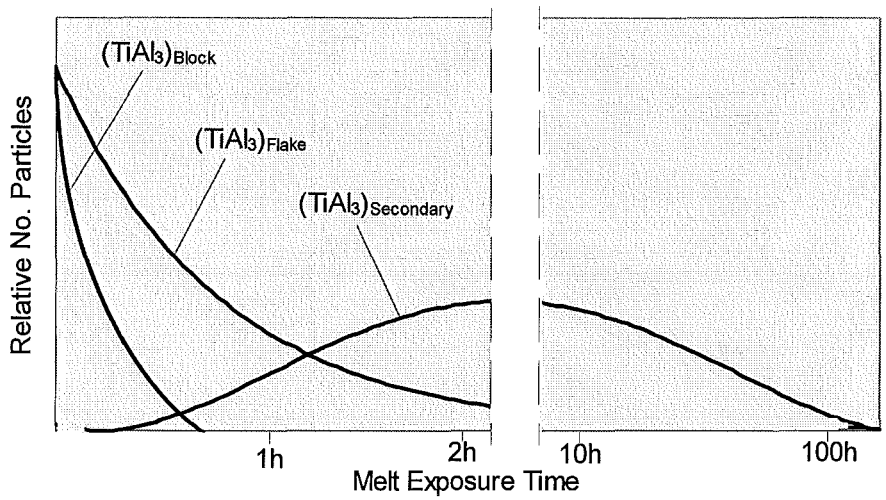


Figure 8: Grain refinement fade characteristics of various titanium aluminides (from Ref. 56).

Arnburg et al[53] calculated that it is highly unlikely that Al_3Ti particles will be completely enveloped in primary (α) aluminium until the peritectic reaction has been triggered on virtually all of the available Al_3Ti crystal boundaries. This was concluded from the fact that the primary (α) layer cannot proceed far via the peritectic transformation due to the slow diffusion of Ti out of the Al_3Ti nuclei. The consequence of this is that each Al_3Ti crystal may nucleate several dendrites.

Earlier studies by St John and Hogan[57] and Banerji et al[58] have investigated the possibility of TiC being the nucleant when less than the peritectic level of titanium exists. While both of these studies found in favour of the TiC theory, the results are not conclusive and the later studies by Arnberg et al[54] found this concept to be incompatible with recorded thermal cooling data. Accordingly TiC is now seldom used as a means of explaining grain refinement results.

Titanium and boron master alloys of varying composition have now replaced titanium only master alloys in most situations. However, titanium grain refining products are still commonly used in the production of alloys for heavily worked wrought products such as thin sheet and cans.

2.3.3 Boron Nucleant Processes

Boron has traditionally been used as a method to remove Ti, V, Cr and Zr from high conductivity aluminium. This process involves the precipitation of mixed borides which agglomerate and settle to the bottom of the melt so allowing later extraction. More recent developments in this area have enabled continuous inoculation by micro-sized boride precipitates which stay in suspension and out of solution so remaining within the final casting[59]. As this latter process is a continuous process, reaction rates must be high between added boron and dissolved titanium, an issue which became important later in this research.

Almost all research carried out prior to 1981 regarding Al grain refinement made note of two important observations which have proved extremely difficult to resolve. Firstly, titanium grain refiners containing boron promoted longer lasting and more effective grain refinement through the formation of AlB_2 and $(Al,Ti)B_2$, and secondly, the addition of boron alone did not cause any detectable refinement irrespective of form or method of boron addition employed. Exceptions to this, which were not fully appreciated at the time were reported by Marcanto and Mondolfo in 1972[60] and Moriceau in 1970[61]; these researchers noted that both TiC and AlB_2 nucleated aluminium in the presence of substantial undercooling. Cornish[62] later noted these findings but did not attempt to associate the implications with any potential industrial applications.

In 1981 Lu et al[63] published a work which has been widely referred to since. This work showed conclusively that boron alone is an extremely potent grain refiner, far more so on a weight basis than titanium. The main results from Lu et al's[63] work are shown in Figure 9.

What Lu et al[63] established was that if undercooling exists, such as in alloys containing substantial Si or Cu, boron in the form of AlB_2 acts as a very strong grain refiner. While the AlB_2 phase acts as a nucleant for aluminium this phase requires undercooling to become active while Al_3Ti does not. As a result any Al_3Ti present will initiate dendrite

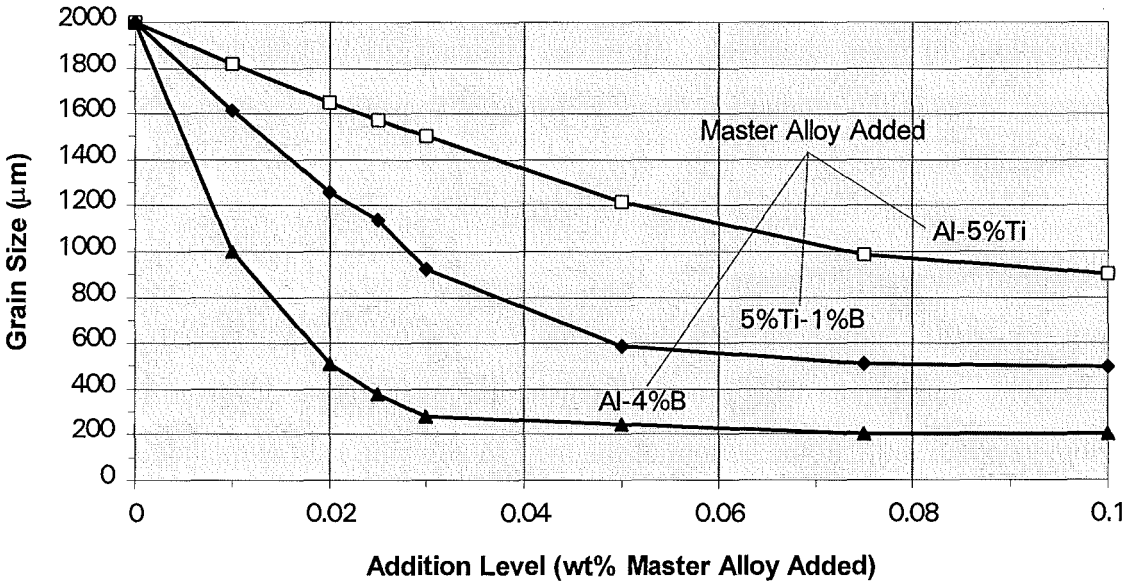


Figure 9: The improved grain refining effectiveness of boron containing and boron-titanium master alloys in Al-7%Si-Mg alloy (from Ref. 63).

growth before the boron phase becomes active. Due to the presence of elements such as silicon, casting alloys almost always experience sufficient undercooling for boron phases to act as strong nuclei. This factor in combination with Lu et al's[63] work has resulted in a number of studies re-examining the grain refinement process in foundry alloys.

Prior to Lu's findings almost all grain refinement investigations centred around wrought alloys which are relatively pure and as a result, the foundry industry was (and still is) using master alloys primarily designed for optimum effectiveness in wrought products. In 1988 Sigworth and Guzowski[64] pointed out some of the disadvantages associated with boron refinement and carried out research into the development of a Ti/B master alloy specifically designed for foundry use. The aim of this work was to produce a master alloy which would avoid boron related problems while maintaining the effectiveness of high boron master alloys (covered below). The detrimental effects they associated with boron are:

- The partial or complete loss of modification in strontium modified alloys- possibly due to a SrB_6 boride forming.

- Boron reacts with titanium forming TiB_2 which settles to the bottom of the furnace, this eventually results in the accumulation of boride sludge deposits.
- The removal of AlB_2 and TiB_2 from the melt due to settling eliminates grain refinement resulting in quite rapid "fade".
- These authors also note that, except in the case of alloys not containing dissolved titanium, no cost advantages seem to exist for the use of boron-only master alloys. (Virtually no secondary metal will meet this criteria.)

A point which is made clear in results published by Vass[55] in 1986 is that when boron alone is present "fade" is extremely rapid, up to eight times faster than experienced with similar levels of titanium alone.

Boron master alloys are available containing AlB_2 or AlB_{12} phases. AlB_{12} type alloys are usually used by primary alloy manufacturers to remove Ti, V, etc and are generally regarded as unsuitable for grain refinement. The alternative AlB_2 alloys are far less common and are supposedly suitable for grain refinement. The results given by Sigworth and Guzowski[64] and others have shown AlB_2 crystals are effective refiners while the AlB_{12} crystal is not. The minor level of refinement which is reported from using AlB_{12} is in fact attributed to the presence of small amounts of AlB_2 within the AlB_{12} alloy.

As mentioned above, TiC has long been thought to be an important nucleant of either $TiAl_3$ or aluminium itself. This has now been largely rejected however with suitable undercooling (as occurs with the commercial foundry alloys) TiC will act as a nucleant in an analogous manner to AlB_2[60].

2.3.4 Titanium -Boron Nucleant Processes

The Al-Ti-B master alloys have been the most common grain refiners in use for several years. Foundry use of these alloys stems directly from their development and use by primary aluminium producers.

5%Ti-1%B Type

The main advantages associated with the Ti/B alloys is an ability to resist fade and promote a finer grain size than that which occurs when similar amounts of titanium alone are used. Figure 9 above shows the response of a 5% Ti - 1% B alloy in comparison to pure titanium and boron alloys. Figure 10 shows the ability of boron-containing master alloys to reduce fade in comparison to pure titanium. The results illustrated in Figure 10 come from work by Guzowski et al[66], who performed tests on 99.7% Al alloy. As mentioned earlier, boron alone will not refine this alloy due to the lack of necessary undercooling.

The most popular Al-Ti-B refinement products are produced in the range 5-6%Ti 0.8-1.5%B, such as KBM Tibor 5:1 and Foseco Nucleant 2.

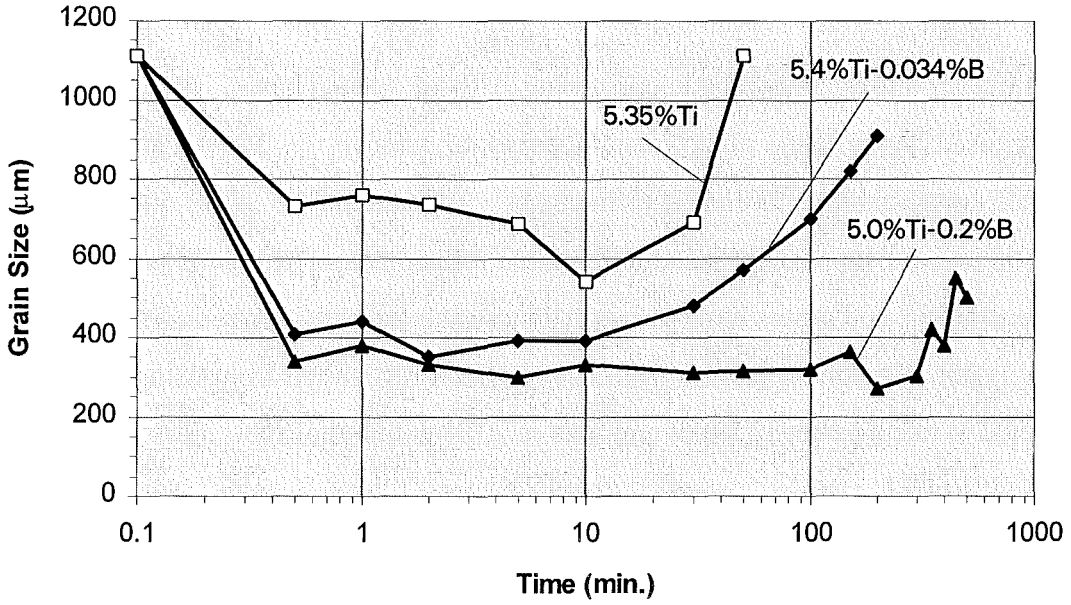


Figure 10: The ability of boron additions to reduce grain refiner fade. (from Ref. 66)

Experimentation on wrought alloys by Marcantonio and Mondolfo[48] published in 1971 found that optimal refinement occurs with a Ti:B ratio of 5; this ratio has subsequently been widely adopted by the wrought and foundry industries. Lower boron alloys are available which reduce the risk of borides collecting in the grain boundaries of thin foil and sheet products[67], however these alloys do not find widespread use in the production of cast products. 3%Ti-1%B alloys are also commonly available and are specifically intended for use in systems which already contain appreciable levels of titanium (as may be encountered with certain secondary alloys).

Several theories have been proposed as to why boron enhances the effects of titanium, the main theories being:

A) The solubility of Al_3Ti is decreased in the presence of boron. Hence, its solution rate is slowed or stopped.

B) Boron somehow nucleates Al_3Ti during solidification.

C) Boron forms a titanium-diboride phase, (TiB_2) which has low solubility in aluminium. The boride phase must then be an effective nucleant for aluminium.

D) A "metastable" diboride phase, $(Al,Ti)B_2$, forms and acts to grain refine aluminium.

In 1987 Guzowski et al[66] showed, with the aid of several other authors' results, that the first two theories are invalid and that neither of the remaining two explain all of the available data. To further complicate matters these authors found that the response of a master alloy is not just dependent on its composition but the morphology of its constituents. The morphology of the borides and aluminides is largely a function of prior master alloy processing, something which has been far from consistent in past research, which highlights the complexity of comparing one author's findings with another. Guzowski also shows that optimal grain refinement of wrought alloys with 5:1 Ti:B master alloys occurs when the boron-containing aluminides have irregular shape and borides embedded in their surface.

Combining results by Arnberg et al[53-56] and Guzowski et al[66] it appears that the borides disrupt the peritectic reaction and transformation resulting in the break down of the aluminides into several small aluminides, so increasing the number of potential nucleation sites and thus promoting a finer grain size. The prolonged life of these nuclei is difficult to explain, however a secondary mechanism (secondary aluminide) becomes active after prolonged melt exposure. The formation of a "secondary aluminide" explains the W-shaped refinement curves reported by Guzowski et al[66] - the initial refinement is caused by the dispersion of Al_3Ti particles, which fade with time but are offset by increasing refinement due to the "secondary aluminides" as proposed by Arnberg et al[53-56].

The question still exists as to what the "secondary aluminides" are. Guzowski et al[66] suggest that the "secondary aluminides" may be $(Ti,Al)B_2$, a nuclei which would not normally be active in wrought products. However, $(Ti,Al)B_2$ will be active in the high titanium regions remaining where Al_3Ti has dissolved by the peritectic transformation. In

support of this theory high titanium regions have been encountered around nucleating diboride particles[61] and previous authors[68,53] have found the diboride phase to become an active nucleant with very minor levels of dissolved titanium present.

As 5:1 type master alloys display no need for undercooling yet perform more effectively than $TiAl_3$ alone, these above theories seem the only current explanation of the characteristics of these alloys.

Work by Lee & Basaran[70] in 1983 indicated that 5:1 Ti:B type master alloys produce grain sizes dependent on the size of the added aluminide particles. As would be expected, smaller particles produced finer grain sizes, however convection was found to be a far more important factor with high convection levels producing very effective refinement.

Early work by Davies et al[71] using a commercial 5:1 Ti:B product illustrated that Al_3Ti nucleates aluminium grains while borides are swept into the grain boundaries. This indicated that not all of the borides were associated with the nucleating phase and that the "secondary" aluminide had yet to form. The question this raises is "What is the effect of uncombined borides collecting in the grain boundaries?" Obviously this occurs when 5:1 Ti:B type alloys are used with only short holding times prior to the activation of the "secondary" aluminide, i.e. it is conceivable that mechanical properties may vary greatly depending on the melt holding time prior to casting.

3%Ti- 3%B

Following Lu et al's[63] work demonstrating the potent nucleating ability of boron master alloys in systems displaying suppressed solidification temperatures, renewed interest was shown in the development of new master alloys specifically for use in the foundry industry. As mentioned above, the majority of foundry alloys display suppressed solidification due to the presence of silicon, thus they are strongly refined by the AlB_2 nuclei. The detrimental factors associated with AlB_2 addition, including cost, do however have the ability to outweigh the potential benefits. This led Sigworth and Guzowski[64] to develop a master alloy containing the mixed $(Ti,Al)B_2$ diboride, which is claimed to: overcome problems of fade associated with 5:1 Ti:B and B master alloys, avoid loss of modification associated with B alloys, and provide finer grain size than either of the two alternative master alloys.

Mondolfo[49] records the undercooling associated with each of the various nuclei as:

Al_3Ti	(0°C)
AlB_2	(1°C)
$(Al,Ti)B_2$	(1°C).

These figures indicate that the AlB_2 and $(Al,Ti)B_2$ phases become active simultaneously, which is exactly what would be expected given the virtually identical forms and lattice parameters of the AlB_2 and TiB_2 crystals. The results given by Sigworth and Guzowski[64] below (Fig. 11) indicate that the $(Ti,Al)B_2$ master alloy promotes a far smaller grain size than AlB_2. It could be assumed that this occurs due to slightly increased numbers of nuclei resulting from the additional titanium present; however this is unlikely as the titanium substitutes for aluminium in the boride rather than providing additional nuclei.

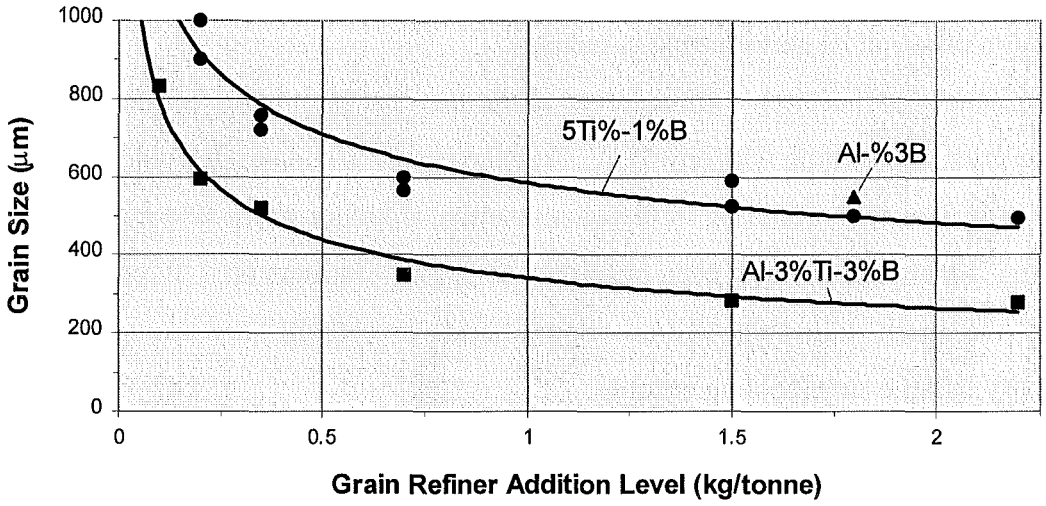


Figure 11: The comparative grain refinement of Al-3%Ti-3%B in Al-7%Si-Mg alloy (from Ref.64)

From Sigworth's results it could be concluded that the enhanced activity of the diboride occurs due to either the slight AlB_2/TiB_2 lattice mismatch or the gradual solution of titanium into the melt. As with the "secondary" boride mentioned earlier, if the latter occurs it is conceivable that the titanium content adjacent to the diboride is substantially higher than that of the overall melt. If the solution of titanium is the reason for enhanced performance the response to diboride additions should prove to be variable with time - something which remains to be verified.

Vass[65] carried out a number of commercial trials to assess the characteristics and viability of Sigworth and Guzowski's[64] 3%Ti-3%B diboride master alloy on a Al-7%Si-Mg (A356)

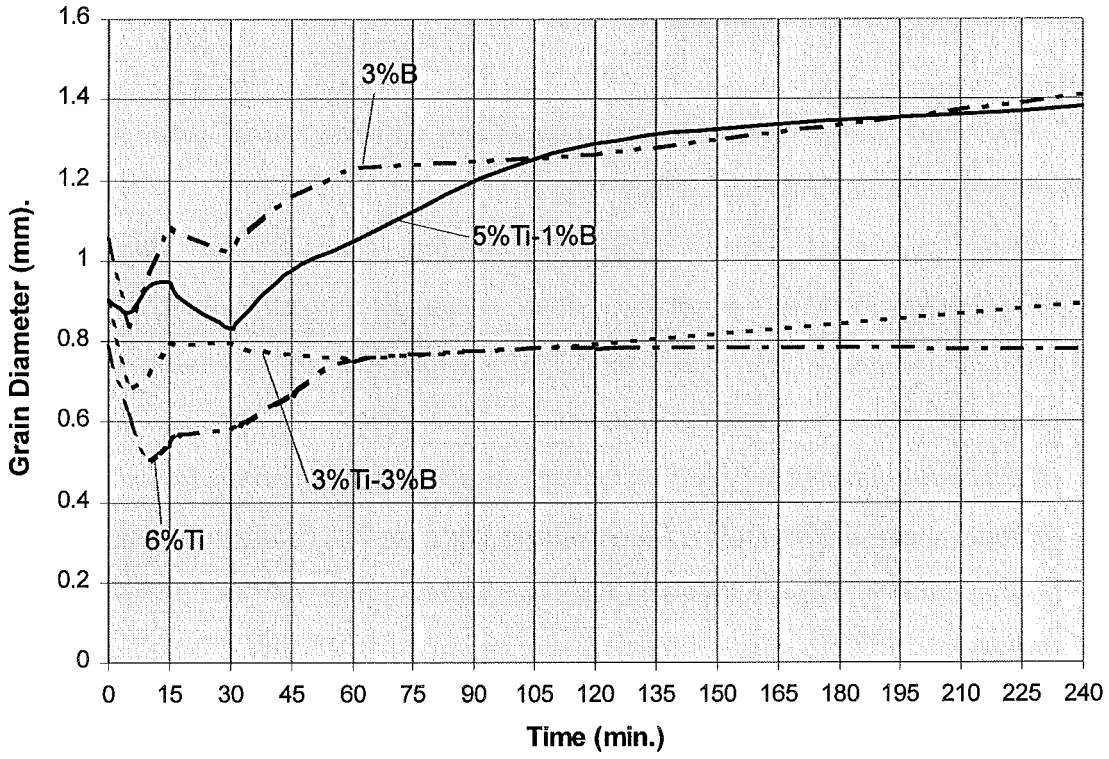
alloy. Some of Vass's[65] results are shown in Figures 12 and 13. It is interesting to observe that several of these "commercial" results do not behave as would be expected given the earlier experimental data, e.g.:

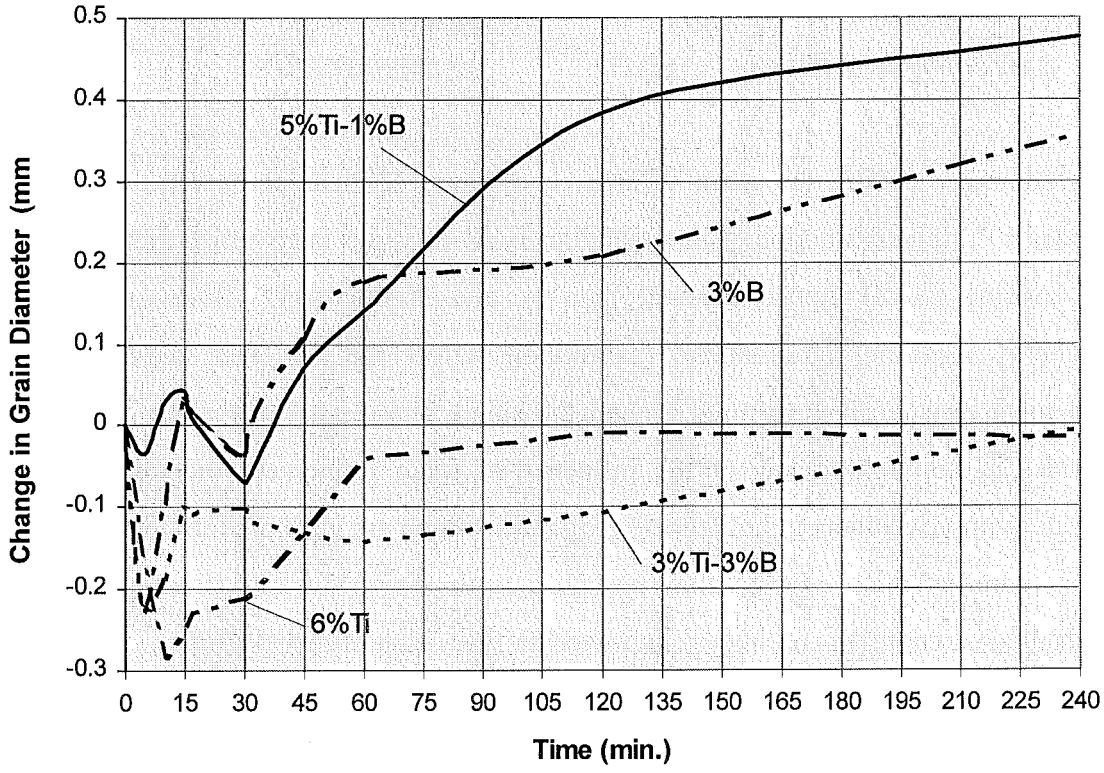
- The titanium promotes a finer grain size than the boron containing alloys when exposed to the melt for between zero and 30 minutes, cf. Figure 9 above.
- Fade of the 5:1 type master alloy is extremely rapid, just as bad as the master alloy of boron alone.

Vass[65] does show that the 3:3 diboride master alloy provides excellent fade resistance and promotes grain sizes almost as fine as those achieved with titanium alone. Based on Sigworth and Guzowski's[64] findings, Kawecki Berylco Alloys (USA) now produces a diboride alloy (3%Ti-3%B) specifically for the foundry industry[73], however to date little information exists on its performance in industry.

An issue which has not been fully resolved is the fact that high boron master alloys fade due to reaction and settling with any Ti, V, Zr, etc present. The diboride could be expected to act in a similar way, resulting in the accumulation of sludge at the bottom of the melt, something which has always been regarded as highly detrimental. It could also be expected that grain refinement and associated boride levels will vary through a casting, particularly in large slow-cooling castings.

Table 1 at the end of Section 2.3 contains the summarised characteristics of the main refiner nuclei mentioned above i.e. the characteristics of Al_3Ti, $(Al,Ti)B_2$, and AlB_2.





Figures 12 and 13: The performance of common grain refinement master alloys following the addition of 0.02wt% of each to Al-7%Si-Mg (from Ref. 65).

2.3.5 The Effects of Grain Refinement

In 1992 Boon and Carver[72] discussed the effects and optimisation of grain refinement. Their summary of grain refinement effects was:

> *"Grain refinement improves the mass feeding characteristics during solidification resulting in reduced total shrinkage porosity as well as promoting a smaller and improved porosity dispersion. In addition a fine grain size results in a smaller and more uniform distribution of secondary intermetallic phases as well as pores resulting from the evolution of dissoluted gas in the melt. The resulting increase in casting integrity is accompanied by improvements in both mechanical properties and pressure tightness.*
>
> *The aesthetics of decorative castings following machining or finishing operations such as anodising are also improved. A fine grain size promotes uniform specular reflectance and eliminates mottling caused by wide variations in grain size."*

This summary covers the main influences of grain refinement however as noted by Gruzleski[18G], the distribution of intermetallics in Al-Si alloys is governed more by dendrite arm spacing (DAS) (hence cooling) than by grain refinement. Boon and Carver's[72] comments regarding intermetallic distribution reflect the fact that large amounts of refinement research have centred around the single phase Al-4%Cu alloy. Gruzleski[18H] provides a thorough review of the influence of grain refinement including comments regarding improvements in hot tearing properties, which are attributed to a lowering of the temperature at which castings may sustain a load. Refined castings are found to gain mechanical strength on cooling at over twice the rate of unrefined examples.

The above comments regarding casting appearance may have seemed unimportant for several products ten years ago but in the current competitive foundry environment any factor which instils the purchaser with confidence in the product is an important marketing tool, due to the perceived improved quality. The appearance of what have previously been regarded as aesthetically unimportant components is assuming ever more significance as

foundries attempt to distinguish their products as superior to those produced by competitors.

It is widely[32,65,72,74,75] regarded that the most important effect of grain refinement is redistribution of porosity and the production of finer and more evenly dispersed voids. While this does not reduce the total volume of porosity, the redistribution usually results in more uniform mechanical properties. Grain refinement is often successfully employed as a means of eliminating gross porosity and associated structurally unsound regions. Improvements in hot tearing resistance and finer pore distributions result in greatly reduced rejection rates due to lack of pressure tightness. Porosity is an important issue for alloys of the eutectic silicon type as these alloys are particularly susceptible to internal shrinkage and subsequent micro- and macro-porosity (See Figure 14 (from Ref. 6)).

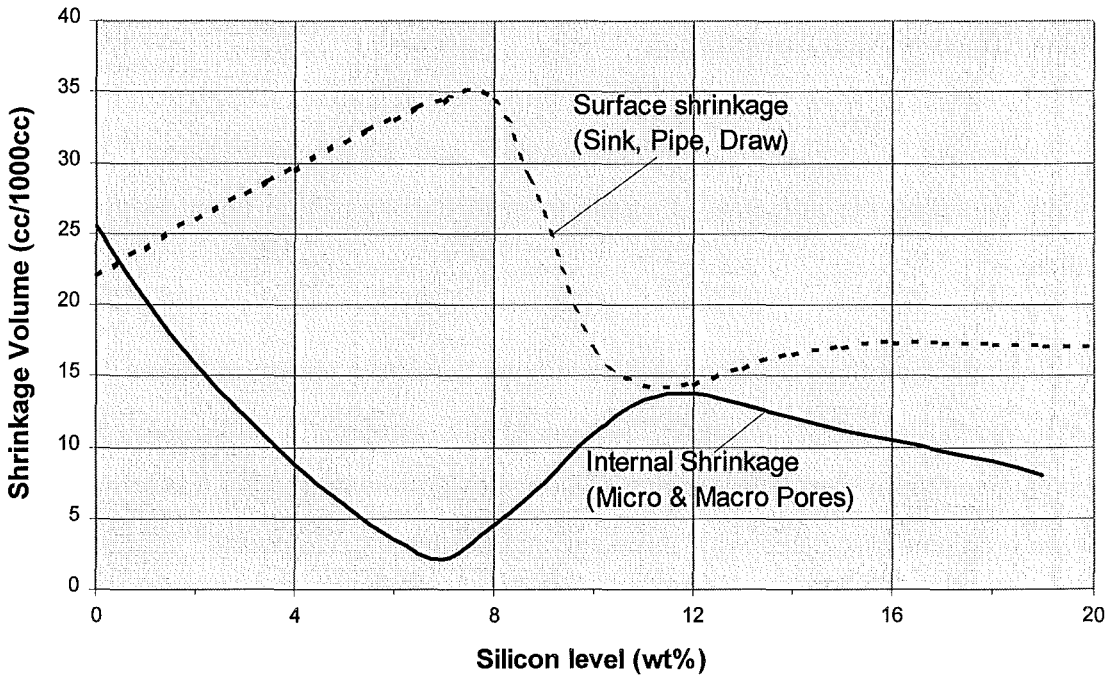


Figure 14: The surface and internal shrinkage of Al-Si alloys (from Ref. 6).

While mechanical properties "of the casting" can be improved dramatically in localised regions subject to porosity, research[32,65,72,74,75] to date has only associated grain refinement with minor increases in the tensile properties of standard test pieces. Vass[65] found no discernible changes in the mechanical properties of his commercially produced specimens. More clinical experiments by Closset[32] indicated that if cooling was slow, as would be

found in sand castings greater than 5 mm thick, grain refinement increases the quality index of Al-7%Si-Mg alloys whilst at faster cooling rates, refinement was found to cause no discernible changes in mechanical properties. It must be noted that none of these reports have dealt with the Al/Si eutectic alloy specifically, they have all centred on Al-Si foundry alloys of the Al-7%Si type.

As Figure 14 indicates, Al-7%Si alloys are more prone to surface shrinkage and less susceptible to internal shrinkage than other common Al-Si alloys. A result of this is that Al-7%Si is the alloy composition least likely to benefit from grain-refinement-induced porosity redistribution. Conversely, the Al-Si eutectic alloy which is subject to approximately five times as much internal shrinkage is far more likely to display property improvements resulting from grain refinement.

2.3.6 The Effects of Melt Constitution

Burt[6], Apelian et al[23], Sigworth and Guzowski[64] and Boone and Carver[72] all make comments regarding the influence of variation in melt composition upon resulting grain refinement.

Burt's[6] findings regarding variations in silicon level have been shown in Figure 14 earlier. Sigworth[64] notes that as silicon levels increase, greater amounts of refiner are required to maintain a given grain size. These higher silicon alloys however, require less refinement to overcome problems associated with shrinkage and hot tearing. Sigworth[64] also states that alloys containing "appreciable" brittle phase such as $FeSiAl_5$ experience negligible improvement in mechanical properties as a result of grain refinement. Apelian et al[23] presents results that indicate that copper has little or no direct effect on grain size while iron is slightly beneficial. Copper and zinc are both found to reduce the effects of conventional refiners. Apelian's comments cannot be viewed as definitive as they come from thermal analysis results rather than direct grain size measurement. Boone and Carver[72] centre on the findings of the above authors but do establish that small additions (e.g. 50 ppm Ti) of AlTiB type grain refiners produce a finer grain size than residual titanium, even when the titanium content exceeds 0.15%. They also conclude that the presence of residual titanium or boron significantly enhances the refinement level caused by subsequent refiner additions.

Table 1: Common Nucleating Agents For The Grain Refinement Of Aluminium

	i	ii	iii	iv
Nucleating Agent **Undercooling** **Addition**	Al_3Ti 0°C Al-5%Ti Al-6%Ti Al-10%Ti + Compressed Powders (e.g. 75%Ti - 25%Al)	Al_3Ti then $(Al,Ti)B_2$* 0°C Al-3%Ti-1%B Al-5%Ti-1%B Al-6%Ti-1%B Al-5%Ti-0.6%B Al-5%Ti-0.2%B Al-5%Ti-0.05%B	$(Al,Ti)B_2$ 4°C Al-3%Ti-3%B Al-2.5%Ti-2.5%B	AlB_2 4°C Al-3%B
Use	Mainly wrought products and older specification alloys.	All alloys.	Foundry alloys, specifically those displaying significant undercooling.	Not used commercially but will act in a similar manner to (iii) (reportedly not as effective as $(Al/Ti)B_2$).
Advantages	Doesn't introduce boron. Proven performance on all alloys. Partial modification of eutectic silicon reported.	Promotes very fine grains in all alloys and avoids the fade associated with Ti only.	Supposedly more efficient refinement of most Al foundry alloys than possible with (ii).	Permanent refinement provided suspension of virtually insoluble AlB_2 is maintained.
Disadvantages	Pronounced fade due to peritectic at 0.15%Ti.	Boron can cause "hard spots" and reductions in the formability of wrought products.	Influence on mechanical properties is virtually unknown but eutectic modification can be lost and borides can cause machining and ductility problems.	Rapid fade due to settling, hence stirring must be provided to maintain the borides in suspension plus problems as per (iii).

* Assuming the "secondary" aluminide is in fact $(Al,Ti)B_2$.

2.4 POROSITY AND DEGASSING

2.4.1 Causes of Porosity

Cracks and voids in castings form by a number of mechanisms, the major processes being: incomplete feeding at the solidification front; restricted thermal contraction within the mould; evolution of occluded gas; and the presence of inclusions such as oxides, sulphides and borides. This last mechanism does not in itself cause porosity but rather it promotes the nucleation and retention of evolved gas. The number of papers and texts written on the subject of porosity in aluminium is immense. As with modification and grain refinement, increased commercial pressure and interest in light alloy quality over the last 10-15 years has resulted in greatly improved knowledge on the subject of porosity formation and eradication.

Incomplete Feeding

Porosity resulting from incomplete feeding can manifest itself in a number of ways from sink, pipe and draw through to micro and macro-porosity. As the process is dependent upon feeding at a micro and macro-scale it is controlled by the solidification characteristics of the individual alloy and the thermal and kinetic characteristics of the mould. As shown earlier by Burt[6] (see Fig. 14) and supported by data supplied by Aluminium Pechiney[76], silicon has a large effect on the propensity of an alloy to form surface or internal shrinkage and hence porosity. As the majority of foundry research has centred around Al-7%Si alloys the higher internal and lower external shrinkage displayed by Al-Si eutectic compositions must always be kept in mind.

Low levels of external shrinkage make the eutectic alloys less susceptible to hot cracking caused by either excessively rigid moulds or stresses within the casting due to non-uniform cooling rates. Since eutectic alloys display this lack of hot cracking plus low shrinkage and very high fluidity,[77] thin walled and complex shapes can be cast to near net shape with relative ease. Al-Si eutectic alloys are however prone to lack of pressure tightness and loss of mechanical integrity due to pronounced internal shrinkage[78]. The design of moulds incorporating adequate supplies of molten metal via exothermic sleeves, shrink bobs, gates and risers is vital, but often not sufficient to eliminate the occurrence of pores caused by inadequate internal feeding of Al-Si eutectic castings. Careful control of solidification patterns through the use of mould chills, feeder placement and varying mould coatings can

help eliminate and determine the final porosity patterns within a casting. Entwistle et al[74] have studied the effects of casting and mould temperatures and occluded gas upon porosity levels and patterns. This work found that the solidification front largely determines the patterns of microporosity within a casting and consequently factors which influence the nature of the solidification front determine the nature of any internal shrinkage present.

Modification and Porosity

Modification is usually associated with increased porosity within the body of a casting (i.e. more micro- and macro-porosity) along with less slump and sink. The latter point may be attributed to lower solidification temperatures and possibly more rapid gains in physical strength as are encountered following grain refinement (mentioned in Section 2.3.5). Traditionally, increased porosity encountered following modification has been attributed to the modifying agents increasing gas levels within the melt. This may possibly occur by one of two means; direct addition of gas present within the modifying agent or the introduction of gas via the mechanics of modifier addition.

It is conceivable that sodium addition may introduce gas directly to a melt, particularly when addition takes place by non-encapsulated pure metal or as sodium salts. Pure sodium and sodium salts have a tendency to be hygroscopic and, if contaminated will release hydrogen when exposed to a melt. Pure sodium is generally stored in a light oil product so that it is protected from the atmosphere. If sodium is added to a melt in this "wet" form vast quantities of hydrogen may be introduced to the melt from the carry-over of seemingly minor levels of residual oil (0.2g oil can produce 350ml of H_2 gas).[27C] A further problem which occurs during the introduction of metallic sodium is that the accompanying violent addition reaction agitates and disturbs the melt surface so providing a means for hydrogen adsorption, and subsequent solution within the molten metal.

Strontium is added almost exclusively as a master alloy which is non-hygroscopic, readily goes into solution and is not associated with excessive disturbance of the melt surface. These factors would suggest that increased porosity due to the addition of strontium might be a result of high hydrogen levels within the master alloy itself.

Work at Alcoa Laboratories[79] has suggested that the addition of strontium increases the pore size and volume fractions without influencing retained hydrogen levels. This work

found that the threshold gas level, above which hydrogen porosity was found, increased with increasing cooling rate. This agrees well with the findings of Dimayuga et al[80], who established that hydrogen is not introduced by the addition of conventional 10%Sr 90%Al master alloys and that provided reactive gases are not utilised to lower excessive gas levels, strontium does not increase the rate of hydrogen absorption or extraction. Continuations of this work generated later publications[81,82] which support the earlier findings and establish that neither melt temperature nor modifier type influence the rate of hydrogen absorption. It is, however, conceded that both sodium and strontium do cause increased microporosity and significantly reduce surface shrinkage. Gruzleski[185] discusses the modifier/porosity interaction in some detail and concludes that the modifying elements change the characteristics of the solidification front so influencing the formation and structure of porosity present. It is also proposed that modification reduces surface tension allowing more and larger pores to form. This latter point is supported by the observation[77] that modification improves mould filling in standard spiral melt fluidity tests. The most significant aspect of the above results is that increased porosity due to modification does not generally originate from directly or indirectly increased hydrogen levels.

The above mentioned findings are in disagreement with work reported by Iwahori et al[83] at Toyota. Iwahori found that sodium causes a redistribution of shrinkage towards internal porosity while strontium does not. It was also reported that strontium prevents the extraction of gas from aluminium subject to a vacuum while sodium does not. The first point is in direct contradiction to Argo and Gruzleski's[82] findings mentioned above and remains unexplained. If strontium prevents the adsorption and subsequent transportation of hydrogen through the molten metal surface as Iwahori's[83] results suggest then the degassing action of inert sparging gases should also be poisoned. This is contradictory to Mulazimoglu et al's[81] report that inert sparging gases are unimpeded by the presence of strontium.

Gas Porosity

It has long been established that molten aluminium absorbs hydrogen, which is later forced out of solution during solidification. Hydrogen is the only gas to cause problems upon casting as it is the only gas to go into solution within molten aluminium to any great extent. The reason that hydrogen causes porosity problems is that the solubility of hydrogen in

solid aluminium is approximately one twentieth of that in molten aluminium. The estimated solubility of hydrogen in the eutectic Al-Si alloy is shown in Figure 15 (this plot originates from results reproduced in numerous publications). The solubility of hydrogen in aluminium is approximately 0.3-0.8cc/100g at typical molten processing temperatures and doubles every ≈110°C above this temperature. During solidification the solubility rapidly drops to ≈0.025cc/100g, whereupon it continues to decrease to minimal levels at room temperature. As occluded gas is ejected from solution it diffuses and combines to form pockets of H_2 gas. The size and number of these pores is governed by the local solidification conditions - slow cooling promotes larger pockets of gas; predominantly within the final regions to solidify.

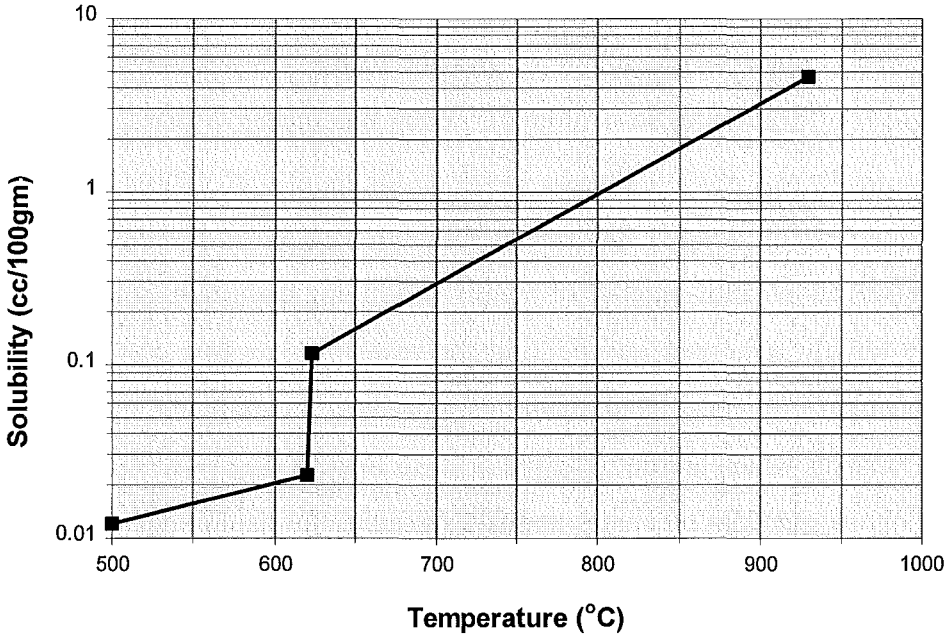


Figure 15: The estimated solubility of hydrogen in aluminium-12%silicon.

As part of the research mentioned above, Entwistle et al[74] found that porosity was undetectable in an Al-8%Si alloy when hydrogen levels were less than 0.1cc H_2 (STP)/100g Al. Conversely, gas levels in excess of 0.7cc H_2 (STP)/100g Al caused porosity to become extensive and evenly distributed. This type of result cannot be widely applied as the degree of supersaturation possible and number of H_2 pores formed is largely dependent on the cooling rate, inclusion content and exact melt composition. A result of this is that the threshold level of hydrogen beyond which porosity is encountered is not easily predicted and will vary from casting to casting as well as from melt to melt. Clegg[37] also quotes maximum permissible hydrogen levels but more importantly notes the effects of various elements on hydrogen solubility. Hydrogen solubility is increased by

elements such as magnesium, lithium, cerium, thorium and titanium and decreased by silicon, copper and tin. Interestingly, many Al-Li alloys can retain up to ten times more hydrogen in solid solution than other commercial alloys, hence lithium alloys are far less susceptible to porosity related problems.[18K] The practical inference from this work is that in most situations hydrogen levels must be kept as low as practicable.

Eastwood published a book in 1946[84] which details the mechanisms and problems associated with hydrogen in aluminium. This early text makes some very significant points which seem to have been largely ignored in later work. Possibly one of the most important regularly overlooked points is that the hydrogen occluded in aluminium is atomic while that rejected and present within ingots is molecular. As Eastwood[84] shows, molecular hydrogen is not a severe source of gas due to low dissociation rates (even at 1200°C only 0.12% of dry hydrogen is atomic). What this means is that "gassy" ingots will not produce melts with high hydrogen levels as the molecular hydrogen within the internal pores cannot easily re-enter the molten solution. This is the reason several early aluminium foundries adopted the practice of rapidly solidifying melts subsequent to molten processing, then rapidly remelting and pouring the relatively gas free cast. The major source of hydrogen porosity encountered with this procedure is entrapment of small, slow-rising hydrogen bubbles which are not released prior to final casting. The slow release of small hydrogen bubbles is what precludes the widespread use of natural degassing prior to casting. Natural degassing involves holding the melt at a low temperature so that a large proportion of the occluded gas is naturally ejected from solution and subsequently released into the atmosphere.

As Eastwood[72] points out, almost all atomic hydrogen which enters a melt does so by the dissociation of moisture at high temperature. This proceeds by one of the following reactions:

$$H_2O \Leftrightarrow 2H + O$$

or $$3H_2O + 2Al \rightarrow Al_2O_3 + 6H.$$

These two reactions are capable of providing far more atomic hydrogen than dry, oxygen free, molecular hydrogen at the same temperature. Damp atmospheres result in rapid saturation of adsorbed atomic hydrogen on the alloy surface and subsequent absorption into the bulk molten metal.

Clearly the best way to prevent hydrogen solution is to prevent the melt being exposed to as many sources of moisture as possible. The most common sources of moisture and hence hydrogen are:

1) Humid atmospheres
2) Products of combustion (e.g. from oil/gas furnaces)
3) Foundry tools
4) Refractories and coatings
5) Corrosion products on initial ingot
6) Damp moulding sands.

Each of these sources must be monitored and controlled as best as possible. Capping compounds which aim to protect the melt surface are discussed in the following section (2.5).

2.4.2 Degassing Methods

In almost all cases, even when molten processing is carried out with due care to minimise the pick up of hydrogen, it is still necessary to reduce gas levels within the melt to avoid gas-related pinhole porosity. As mentioned above, two techniques which have been used to lower hydrogen levels are natural degassing and allowing the melt to solidify prior to rapid reheating and casting. Apart from being prohibitively slow, these methods are extremely expensive due to high energy requirements.

All hydrogen removal methods currently employed industrially involve subjecting a melt surface to an atmosphere containing little or no hydrogen. These methods include vacuum degassing and the introduction of inert and/or reactive gases. Both Clegg[37] and Hoffman[85] published papers in 1986 which outline most common degassing methods used including "in-line" treatments and those performed on a batch basis. The least common of the above processes is vacuum degassing which, as the name suggests, relies on vacuum extraction of hydrogen from the melt surface. Subjecting the melt surface to a vacuum lowers the concentration of hydrogen at the melt surface so lowering the equilibrium melt hydrogen level and driving excess hydrogen from solution. The vacuum also allows hydrogen pores to expand so increasing their buoyancy and hastening their ascent and release through the

melt surface. This secondary effect is dependent upon not only the absolute pressure but the metallostatic head and rate of pore nucleation. The deeper the melt, the less the vacuum increases the pore rise velocity. With an atmospheric pressure of 100mm Hg, bubbles at a depth of 1m will rise ≈23% faster than those under standard atmospheric pressure, the bubbles approaching the melt surface will move ≈40% faster (see Appendix C). With an absolute pressure of 100mm Hg the optimum increase in degassing rate is 35-38%; with 10mm Hg the corresponding increase is 95-105%. It would be interesting to monitor the importance of this mechanism in comparison to atomic hydrogen diffusion and direct extraction via the melt surface. It would also be of interest to examine the influence of pore nucleant levels (e.g. inclusions) as no information seems to exist on these issues.

The main industrial users of vacuum degassing are large foundries in Europe and Japan producing large volumes of high quality castings. The high capital cost involved with the equipment required for this gas extraction technique has made it unviable for most foundries and as a result the use of this process is likely to remain limited.

Purge/Sparging Gas Methods

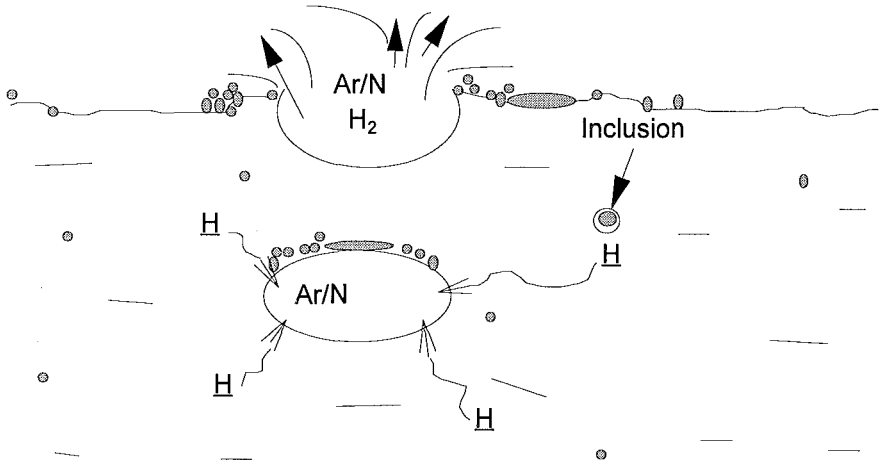


Figure 16: The mechanics of inert gas degassing.

Most degassing processes involve the introduction of a sparging gas to the melt: these gases may be reactive or inert. Reactive gases such as chlorine and fluorine actively bond with the atomic hydrogen, rapidly flushing it from the melt as a combined gas. When inert gases such as argon and nitrogen are bubbled through the melt, they provide a surface (the bubble surface) free of hydrogen through which the occluded hydrogen can diffuse. Once within the rising bubble the atomic hydrogen rapidly combines to form molecular

hydrogen which is subsequently released into the atmosphere when the sparging gas bubble breaks the melt surface. This is illustrated in Figure 16. Another advantageous action of the rising gas bubbles is that they tend to sweep inclusions to the surface which are then combined in the surface dross.

One of the oldest methods used to introduce sparging gases to a melt has been to plunge tablets of hexachloroethane below the melt surface, which rapidly break down effervescing chlorine. Similar tablets are available which release nitrogen or fluorine into the melt. Gases may also be added directly by injection via various lances, porous plugs and rotary impellers. Since the hydrogen removal rate is determined by the surface area of purging gas available methods which generate finer bubble dispersions are both more efficient and faster acting. Gas introduction by submerged impeller methods generate possibly the finest bubble sizes while not being prohibitively expensive to implement. Consequently, this method of gas introduction has found favour worldwide in all types and sizes of aluminium foundries. Companies such as Foseco produce ranges of proprietary rotary impeller degassers and have published several accounts of the design and successful implementation of these units into foundries of varying size and type[86,87,88]. The schematic layout of a typical impeller unit is shown in Figure 17 (the baffle plates act to reduce swirling and melt surface disturbance).

The advantages of rotary impeller degassing can be summarised as follows:

- Low treatment cost.
- High efficiency ensures short degassing times (typically 5-8 min) and lower final gas contents than possible with methods such as simple lance injection.
- Initial capital outlay is not beyond small foundries.
- The process may largely be automated so that consistency in gas levels and treatment times (hence composition) may be achieved.
- Skilled operators are not required.
- Pollution is non-existent (provided certain reactive gases are not used).

Lamont[89] details the introduction of this method of degassing at Ford's Alloy Wheel Plant in Auckland, NZ. Rotary degassing replaced a nitrogen flux injection process and was accompanied by: a decrease in processing cost of 44%, reduced reject castings due to

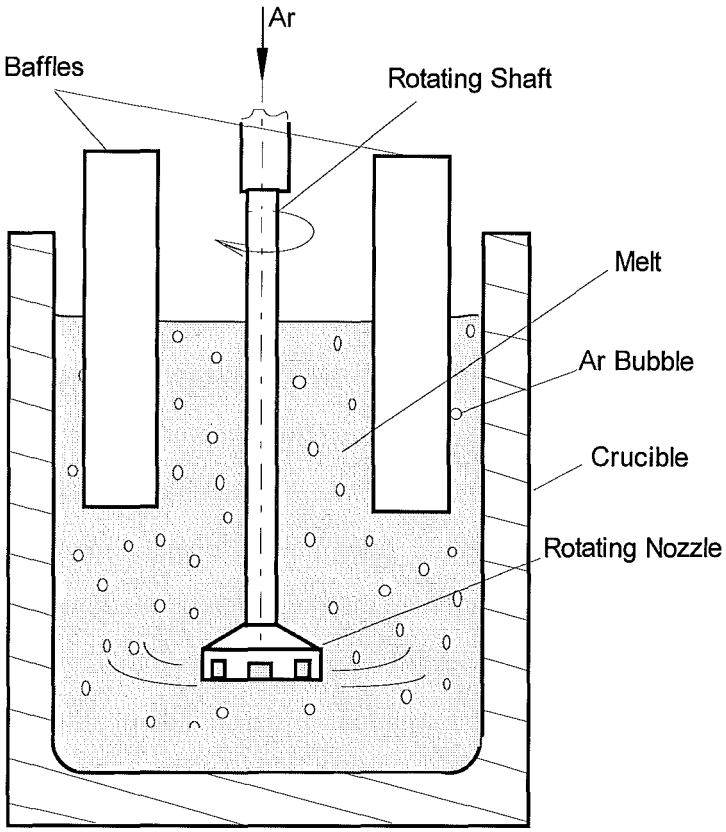


Figure 17: The layout of a conventional rotary impeller degasser.

micro-porosity, faster treatment times and process consistency to a point where statistical process control could be implemented.

Flux injection usually involves the simultaneous injection of sparging gas as well as agents to flux, modify and/or grain refine the melt. This is usually carried out using an open ended lance. In certain instances flux injection can be highly advantageous as fluxing agents may be introduced which perform functions such as the removal of prior modifiers and introduction of phosphorus to hypoeutectic alloys. Fenyes et al[90] reported that flux injection can produce melt covering fluxes which are far drier (contain less unoxidised aluminium) than those produced by "conventional" fluxing methods. An example is then given of a foundry employing this degassing/cleaning technique which projected savings of up to $US 25,000 per annum simply due to reduced metal loss within the cover dross.

Several reports have shown significant improvements in degassing effectiveness when reactive gases or mixes of inert and reactive gases replace the use of inert gases alone. By

developing a theoretical model of the bubble degassing mechanism Sigworth[91] has shown that in certain instances the halides double the mass transfer coefficient at the bubble surface. He does note however that when small bubbles are generated, such as with rotary degassing, the hydrogen removal rate is not limited by mass transfer into the bubble, hence the reactive gases provide no real advantage. This theoretical quantitative analysis indicated that by far the most significant factor in degassing is in fact bubble size.

Increasingly, chlorine and several other reactive degassers such as "freon"[†] are being phased out due to their detrimental environmental effects. This has led to the development of non-harmful replacements such as sulphur hexafluoride (SF_6), which is available as a direct substitute for most other forms of reactive gas addition. Saha and Fay[92] detail the introduction of SF_6 which has an added benefit over freon in that it has a lower surface tension resulting in finer bubbles and more effective degassing and flushing of inclusions to the melt surface.

One of the major problems associated with degassing is variation in the melt composition due to either direct reaction with purge gases or increased vaporisation into the flushing bubbles. Some relevant elements which are particularly sensitive in this regard are sodium, strontium, calcium and magnesium. In the case of sodium, the rate at which extraction takes place is so high that this element is often completely eliminated irrespective of the degassing means employed. Strontium is also subject to loss but this effect is only severe in the presence of reactive gases. A result of this is that sodium modification can not be performed prior to degassing unless initial sodium levels are extremely high; thus, as mentioned earlier, it is highly unusual to purchase sodium premodified ingot. Since inert degassing may be used with strontium premodified ingot without severe modifier loss the introduction of additional modifier in the foundry is often unnecessary. When reactive gases are employed, strontium will in fact be removed before hydrogen, thus reactive gases are not compatible with strontium premodified ingot. Antimony modification is unaffected by exposure to either reactive or inert gases and so may be used with either successfully. Whilst not common, calcium modification is also incompatible with the presence of

[†] Du Pont Trademark - Dichlorodifluoromethane (CCl_2F_2).
* Discussed in Section 2.8.

reactive gas. Magnesium is also removed from the melt by reactive gases and in fact, the addition of chlorine is the principal method of magnesium extraction used.[93]

On line degassing methods such as "MINT" and "ALPUR" have not been covered in this review although Clegg[37] does provide comments and references regarding these processes.

2.4.3 Measuring Gas Contents

Numerous attempts have been made to develop hydrogen analysis techniques to measure and control the effectiveness of degassing methods and to establishing the propensity of a melt to form voids. The techniques available can be separated into two distinct groups; those which are intended for rapid qualitative or quantitative analysis within the foundry and those which provide highly accurate quantitative results following stringent and protracted processing within a laboratory. The latter methods include subfusion and vacuum fusion while the former include vacuum solidification, density measurement, circulating gas equilibrium and vacuum solidification gas evolution. A useful review concerning the analysis techniques commonly employed commercially was published in 1989 by Acklin and Davidson.[82]

Advanced Techniques

During these methods hydrogen is vacuum extracted from specially prepared hot (subfusion or Ransley method) or molten (vacuum fusion) samples. The hydrogen is then allowed to diffuse through a heated palladium tube into a chamber where the hydrogen concentration is determined by pressure rise or some other relevant physical measurement. Due to the expense, need for skilled personnel and time required to carry out these analyses they are usually only conducted as a means to assess and calibrate the effectiveness of more rapid foundry based methods. These processes are briefly outlined by Gruzleski[16L] with more detailed information available through companies such as Leco.

Vacuum Solidification Methods

As mentioned above with regard to vacuum degassing, gas solubility decreases and evolved pores expand when the melt surface is subjected to reduced pressure. Hence, when metal is solidified under a vacuum, gas-induced porosity is accentuated. Physically, this means that variation in gas content is also accentuated, so easing differentiation between

various gas contents. This process is the basis for the most wide ranging and common forms of gas analysis. The oldest and simplest of these methods involves solidifying a small sample (≈ 50-100ml) in a metal cup then observing the expansion of the melt surface. This is sometimes referred to as a Straube-Pfeiffer test. In this test, gas-free melt surfaces will remain flat or slightly concave (due to thermal contraction) as the metal will not contain pores to expand within the casting. Gassy melts produce expanded convex surfaces with a "cauliflower" type appearance. The real advantages of this test and all commercial reduced pressure tests is that they can be carried out in the foundry and generate results prior to cast pouring, so that problems may be identified and corrected before defective components are produced.

A slight variation on the above process is to section the vacuum-solidified samples so as to gain a better impression of exactly what level of porosity exists. Standards have been produced to quantify hydrogen levels by the extent of porosity displayed on sectioned surfaces[94,95]. However, the accuracy of actual hydrogen levels gained by these means are dubious at best. The reason these standards are severely compromised is not just that they are dependent on visual comparison, but that porosity is strongly influenced by factors such as: composition; sampling temperature; the exact vacuum level attained and inclusion levels. The action of inclusions as nucleating agents for gas pores is critical and as pointed out by Miller[96] in 1986, if inclusions are eliminated, vacuum tests become largely ineffective. Miller illustrated that in the absence of inclusions vibration may be used to reduce pore formation, although this does not seem to have been adopted commercially. The conclusion must therefore be drawn that porosity within vacuum-solidified samples (and all samples for that matter) is a measure of the *hydrogen and inclusion* levels within a melt and is a true measure of the propensity of a melt to form hydrogen voids. The result of this is that if hydrogen levels are measured by a more specific means as well as by vacuum solidification, an indication of the inclusion levels can also be obtained.

The acceptable implementation of reduced pressure tests (RPTs) was the subject of a series of papers by Rasmussen et al[97,98], who stressed the need for complete consistency if RPTs are to yield any form of quantitative information.

Another development of the RPT test is to measure the density of vacuum-solidified samples. This procedure was described by Rosenthal and Lipson[99] in 1955 and is subject to the same problems as all RPT tests outlined above. One of the other major problems associated with this process is the wide variation in sample density caused by compositional variation within certain alloy specifications. Density tests to determine porosity content were initially attempted by Ohira and Kondic[100] in 1954. However, they did not employ vacuum solidification to accentuate the gassing effects and as a result, their process was regarded as insensitive and of no industrial significance. A limitation with RPT density tests is that open pores and gas which evolves from the melt during solidification are not accounted for within the density measurements. To offset this problem Rooy and Fischer[101] suggest that a vacuum no greater than 500mm Hg be employed, but this limits the resolution to which varying porosity levels may be determined. An alternative test method which avoids open pores without limiting the vacuum and hence resolution, is the production of RPT castings which are fed from oversize risers and are not exposed directly to the melt surface. This method was developed in 1959 by Sulinski and Lipson[102] who developed moulds of known constant volume with excessive risers which could easily be removed. Sulinski and Lipson's[89] moulds produced castings of constant volume, therefore weighing the samples was sufficient to determine the density and likelihood of castings being gassy. Being simple and fast, this type of test has found some commercial success. In 1970 Church and Herrick[103] reported that with very minor changes, Sulinski and Lipson's[89] original method was being used commercially with excellent correlations being obtained between RPT gas predictions and actual casting porosity as determined by radiographic inspection. These authors[103] also noted that actual porosity levels vary so widely from one casting type and layout to another that radiographic results and actual porosity levels can only be predicted given prior correlation data.

The last and possibly most common quantitative RPT test is the initial bubble test (Dardel's Test[104]). This test relies on observing the melt surface during solidification and monitoring the time and vacuum required for the first bubble to emerge. The test results are usually presented as the absolute pressure at which the first bubble appears. Rooy and Fischer[101] suggest that for sound sand castings, 100mm Hg is a suitable vacuum level, while 5mm Hg or lower may be required if premium quality castings are being produced.

Calculations can be performed using Sievert's Law to relate the vacuum results to theoretical hydrogen levels[18M]. Once again this test ignores the critical influence of inclusions on bubble formation and so seldom generates accurate results.

Circulating Gas and Other Techniques

The removal and monitoring of occluded hydrogen from aluminium is a problem not only in the foundry but also at the source of primary aluminium. Smelters have sought to monitor and control hydrogen mainly so as to minimise defects in wrought products. The large resources of these organisations have resulted in the development of measurement techniques which have subsequently been marketed and developed for use in foundries of virtually any size.

Alcoa has marketed a hydrogen analyser for use in the primary metal industry since the mid sixties. This product uses principles and equipment originally designed by Ransley et al in 1958[105]. The Alcoa product is marketed under the "Telegas" name and relies on circulating a small volume of inert gas (N_2) through the melt until an equilibrium state is reached. Sievert's Equation is then applied relating the entrained molecular hydrogen pressure to the dissolved hydrogen concentration. A katharometer is used to measure the amount of entrained hydrogen within the circulating nitrogen, with the resistance measured by this device easily converted to melt hydrogen concentration. This method of gas analysis is not greatly influenced by inclusion level and so gives a true account of the actual melt hydrogen level.

"Telegas" units have proven to be accurate and reliable enough to find use throughout the aluminium industry, particularly following revision of the original hardware in 1985. These improvements along with the development and use of "Telegas" are detailed in a 1986 paper by Granger[106]. Alcan also market a hydrogen analyser which works on the same principles as "Telegas". The Alcan unit is marketed under the "AlScan"name and has been available since 1989[107]. AlScan incorporates corrections to the hydrogen readings dependent on the type of alloy being processed and utilises more robust sampling probes than "Telegas".

Gas analysers which work on a completely different principle to the Alcan and Alcoa products are produced by Severn Science (Instruments) Limited (UK). The Severn equipment works as follows: *"A constant mass of melt (100g) is placed in a chamber and the pressure is reduced rapidly to a predetermined value by a vacuum pump. The chamber and associated vacuum system is then isolated from the pump and the sample allowed to solidify. As the melt cools hydrogen is released and its partial pressure is measured by a calibrated Pirani gauge whose output is converted continuously to a digital display of hydrogen content."*[108] This procedure was devised to allow rapid and accurate results to be achieved on the foundry floor while employing simple-to-use equipment. Actual production experience with this equipment[110] has shown that problems arise in maintaining an accurate calibration (by keeping the vacuum chamber hot and free of moisture) without the electronics overheating. The influence of melt cleanliness and pore nucleation upon gas release, and hence the accuracy of the Severn equipment, does not seem to have been reported. This last issue may require addressing, as may the effects of compositional variation, before the output from this equipment can be regarded as accurate.

Acoustic emission during solidification has been investigated by Swiss Researchers[109] in the hope that sound emitted during pore formation may form the basis for future quantitative metal analysis. Three distinct types of noise were recorded, which may enable differentiation between various pore types, e.g. shrinkage, gas, etc and quantification of the amount of each. As yet no commercial development of this concept would seem to have evolved.

Shrinkage Effects on Gas Porosity

Traditionally, the appearance of porosity has been attributed to either rejection of occluded hydrogen or solidification shrinkage caused by a density difference between the solid and liquid phases. Inclusions assist the nucleation of pores but do not in themselves create porosity, so their influence has not been fully appreciated until recent years. Porosity is almost always most prevalent in regions susceptible to shrinkage stresses. Early work, such as the 1946 text by Eastwood[84], tried to delineate the various causes and characteristics of different types of porosity, mainly on a basis of appearance. Although in some instances this is possible, most commercial foundry alloys do not produce such clear-cut results. Whilst pipe and hot cracking are clearly associated with shrinkage, as are most

large macro-pores, micro-porosity is often ambiguous in origin. Most conjecture relating to these pores has concluded that micro-pores are the result of both shrinkage and hydrogen, the two processes working together with the shrinkage component particularly influential in slow cooling regions.

Results by Entwistle et al[74], who monitored pore distribution in an Al-8Si alloy, showed that: *"If the gas level is too high shrinkage is of little importance in determining porosity formation; if the gas level is too low the solidification shrinkage itself is ineffective in producing pores. The interesting feature of porosity is that, in the intermediate range although both gas and shrinkage act together, it is apparently the shrinkage (and the solidification mechanism) which determines where pores form and their total volume."* These results clearly indicate that shrinkage is only significant for intermediate gas levels (0.15-0.45ml H_2/100g Al).

Attempts to resolve the issue of shrinkage verses gas porosity have included several numerical models calculating the magnitude of localised pressure drop due to shrinkage and how this influences pore formation and hydrogen extraction. One of the most recent publications concerning a detailed computational model was produced by Carpenter et al[111] in 1993. Carpenter's[111] model was designed to represent sand cast Al-7%Si alloy and took account of coupled heat, mass and momentum transport phenomena. An Al-7%Si alloy containing 0.17ml H_2/100g Al displayed micro-pores, whereas Carpenter's numerical model indicated that the pressure drop due to shrinkage would be far too low to account for pore formation. Carpenter et al[111] then showed that pressure drops resulting from shrinkage have virtually no effect on micro-pore formation and that hydrogen segregation is the dominant factor in pore formation under sand cast conditions.

Given the above results, it could be assumed that micro-porosity with most sand cast Al-Si foundry alloys is controlled almost exclusively by hydrogen level and not shrinkage. It must however be remembered that alloys of both higher and lower silicon level than investigated by Carpenter[111] and Entwhistle[74] are subject to higher levels of internal shrinkage.

Porosity Elimination

One process which has been developed and used successfully to eliminate porosity is hot isostatic pressing (HIPing). HIPing is often portrayed as a complete solution to porosity induced problems[119]. Unfortunately this is not completely true. HIPing is a process whereby components are subjected to high isostatic pressures at elevated temperatures. The combined effects of high pressure and elevated temperatures act to close internal pores in the cast material. Work by Wakefield[120] in 1993 has shown that while HIPing can improve mechanical properties it is also associated with increased property variance, so resulting gains in design strength are minimal. Increased variability was proven to result from entrapped oxides which had nucleated porosity and then been encased within the alloy in a compressed high stress concentration form. Filtration to eliminate oxides was not found to be a satisfactory solution as 'super' clean metal was required to completely eliminate entrapped oxides. The filtered metal did, however, reduce the need for subsequent HIPing and also improved casting consistency.

2.4.4 The Effects of Porosity

- *Positive Effects*

  Porosity has several effects on cast aluminium alloys, not all of them being detrimental. The positive influences of gas pores include reduced shrinkage, and at levels above ≈0.5ml H_2/100g Al, a more even pore distribution which often eliminates macro-porosity in poorly fed regions. With alloys or castings which are subject to feeding problems, increased total pore content with an associated redistribution of porosity can lead to elimination of hot tearing and unsound gross porosity regions. This can result in castings which are dimensionally and mechanically superior to lower gas content equivalents. The main uses for intentionally high gas content castings are ornamental and non-critical, low stress applications. These items are generally of low value hence savings in riser material can become a significant economic issue.

  The addition of hydrogen to a melt may be accomplished by various means with the addition of anhydrous ammonia[112] being one of the more preferable. Ammonia may be added directly via conventional gas lance or impeller equipment. This process is clearly preferable to some of the more traditional techniques such as the

addition of green wood, potatoes and boiling fluxes as it affords the foundryperson far greater process control and consistency.

- *Negative Effects*

  The advantages of porosity are almost always outweighed by the detrimental effects, these being: reduced impact and fatigue properties; possible loss of pressure tightness; decreased mechanical properties and unacceptable aesthetics. Porosity not only limits attainable mechanical properties, it causes far greater scatter in recorded properties.

  The influence of pores on the fatigue and impact properties is not well documented. However, results from a 1984 study by Wickberg et al[113] show that the effects are detrimental, as would be expected. Unfortunately, these results show significant scatter and are not plentiful enough to generate statistically significant results. The formation of continuous voids which cause loss of pressure tightness is also not well reported. Due to the requirement for voids to be interconnected it is conceivable that shrinkage, cracking and macro-pores, along with entrapped oxide films, are more likely to be the cause of this problem than gas. In a clean melt it is difficult to imagine how micro-pores due to hydrogen could increase the instance of "leaker" castings (non-gas-tight castings).

Published results relating the mechanical properties of Al-Si eutectic alloys to gas porosity have not been found, although several authors[89,116,117,118,119] have concentrated on gas porosity in Al-7%Si-Mg alloys. None of these papers present results using similar porosity reference scales (e.g. H_2 content, pore volume, pore area, etc) so direct comparison of the results is difficult. Consensus would appear to be that ductility is as much as halved with high gas contents (≥5 vol.% porosity) while tensile and proof strengths are reduced by 10-15% and 5-9% respectively for similar gas levels.

One area of porosity influence which has been the subject of several technical reports is the associated decrease in tensile properties. Work at the University of Canterbury[114] has shown that pores resulting predominantly from shrinkage are far more deleterious to tensile properties than gas pores. A set of experiments which concentrated on shrinkage porosity was reported by Herrera and Kondic[115] in 1977. This research centred around LM6 and

LM13 alloys and included a number of results relating the influence of pore length, pore area at fracture and volume porosity to the tensile properties. What is clear from this work is that measurements of the area porosity correlate well to the mechanical properties whereas those based on density measurement do not. This finding could be attributed to the non-uniform density of the samples used, however the same conclusion was reached by Surappa et al[116], who studied uniform gas porosity in Al-7Si-Mg alloys. Herrera and Kondic concluded that LM6 tensile and proof strengths are not effected by porosity to the same extent as ductility yet the detrimental effects are significant in each case, which is not surprising given the extent of porosity within the samples they investigated (typically ≈20% of the sample cross-sectional area!).

As pointed out earlier, aesthetic standards for castings of every type are now extremely high. As a result of this, exposed porosity is often regarded as unacceptable even though it may not compromise the functionality of the casting in any way. Provided macro-porosity and cracks are not present, the major casting regions to expose porosity are machined surfaces, hence it may be preferable to avoid porosity in areas subject to machining by compromising other areas. A point which has been made in the literature[89] is that exposed micro-porosity on surfaces to be painted will often cause significant paint bubbling due to gas expansion during any later paint baking or heat treatment processes.

2.5 FILTRATION AND FLUXING

2.5.1 Inclusion Sources and Effects

The influence of inclusions upon the casting process and final product characteristics has only been fully appreciated in the last ten to fifteen years, hence almost all literature on this issue has been published within this period. The bulk of research on molten aluminium reported in recent years has concentrated on inclusion monitoring, control and elimination (via filtration and fluxing) along with the introduction of inter-related foundry-based rotary degassing units.

Inclusion Sources

Inclusions present in final castings come from a number of sources including suspended dross, refractory degradation, undissolved hardeners and pieces of eroded mould. These particles may enter the molten alloy at any stage of processing from the primary smelter cell through to the final mould cavity, thus control of contamination is receiving attention industry-wide. An extensive list of commonly found inclusions was published by Apelian and Shivkumar[121] in 1989; a summarised version of this table from a later paper by Apelian[122] is shown in Table 2.

Table 2: Typical Inclusions in Aluminium Foundry Alloys (from Ref. 122)

Type	Formula	Morphology	Density(g/cm^3)	Dimensions(μm)
Oxides	Al_2O_3	Particles & Skins	3.97	0.2-30
	MgO	Particles & Skins	3.58	10-5000
	$MgAl_2O_4$	Particles & Skins	3.6	0.1-5
	SiO_2	Particles	2.66	0.5-5
Salts	Chlorides	Particles	1.98-2.16	0.1-5
Carbides	Al_4C_3	Particles	2.36	0.5-25
	SiC	Particles	3.22	
Nitrides	AlN	Particles & Skins	3.26	10-50
Borides	TiB_2	Particle Clusters	4.5	1-30
	AlB_2	Particles	3.19	0.3-3
Sludge	Al(FeMnCr)Si	Particles	>4.0	

Inclusions can be either solid or liquid within the solidifying alloy, with those associated with halides generally being liquid. As mentioned in the preceding section, halides such as chlorine and fluorine are added as reactive agents to remove hydrogen. They have the ability to enhance inert gas degassing and to improve inclusion removal. This occurs due to a reduction in the surface tension of gas bubbles and the formation of fluxing agents on the melt surface which readily incorporate any inclusions brought to the melt surface.

A theoretical numerical analysis of the process of inclusion removal by gas bubble flotation was carried out by Martins et al[123]. This study established that during degassing, inclusions are exposed to the melt surface each 1 to 10 minutes. This suggests that clean melts should be obtained within the five to ten minutes over which degassing is performed. In reality this is not the case, which may be a result of either the melt continually oxidising and so forming new inclusions or inclusions failing to be incorporated into the dross once they reach the melt surface. Martins et al[123] noted findings of earlier research which established the ability of halogen salts to effectively wet inclusions. This supports the theory that the halides enhance dross inclusion retention and so improve inclusion removal rates and melt cleanliness.

Most Rotary Degassing Units (RDUs) achieve close to 100% efficiency with bubble sizes of around 5mm diameter; accordingly these systems have shown no benefits in hydrogen removal when finer bubbles are used. When flotation fluxing is considered, finer bubbles produce better cleaning and increase the removal of very fine inclusions which are difficult to extract by filtration. It has been mentioned earlier (Section 2.4.2) that sulphur, when added via SF_6, also lowers melt surface tension and in so doing refines the evolved gas bubble size. This action should result in the enhanced removal of inclusions as well as improved degassing when bubble sizes exceed ≈5mm diameter.

Since halides can act as sources of liquid impurities, their use is limited for reasons other than environmental concern. It has been reported[124] that to minimise contamination and the attack on carbon-containing equipment while retaining the beneficial surface effects of fluorine and chlorine, fluxing gases should not exceed 10% by volume of halogens. When alloys containing magnesium are being processed, even lower halide (<5% vol.) levels are advised. Other recommended procedures to minimise detrimental halogen effects include minimising residual sodium, calcium, potassium and lithium levels prior to fluxing and minimising the degree of superheat used during molten metal processing.

Solid inclusions consist of particles entrained from exogenous sources and those formed in-situ. The former type come mainly from refractories and moulding sands and as a result, may be incorporated into the alloy anywhere from smelter pot line through to downstream of the last fluxing and filtration operations. The inclusions which form within

the melt itself consist mainly of oxides of aluminium and magnesium and naturally form at each stage of melt handling. Since oxidation of aluminium is unavoidable, melt charge stock will inherently contain oxidised surfaces which act as potential inclusion sources; anodised products are particularly potent in this regard. During processing the oxide film which forms is relatively dense and continuous and thus acts to protect the bulk of the melt from further oxidation. When the melt surface is broken by skimming, degassing or ladling, further oxidation rapidly takes place. The rate of this oxidation is temperature and composition dependent with thick oxides forming virtually instantly above 780°C, a problem which is exacerbated by the presence of magnesium.

The addition of magnesium is a potentially major source of oxide contamination. If magnesium is allowed to flare-off on the melt surface, fine particles of magnesia (MgO) form as a white fume which in turn promotes the formation of highly detrimental spinel ($MgAlO_4$). Both magnesia and spinel formation is dealt with in some detail in a paper by Echhert[125], who also points out that boron-containing compounds greatly reduce oxidation and hence the creation of potential oxide inclusions. Unfortunately, boron additions themselves tend to result in the addition of substantial boride inclusion clusters which act in a detrimental manner as do most inclusions.

Corundum (Al_2O_3) is an inclusion which can form due to a reaction between aluminium and refractories containing appreciable silicon, most likely by the reaction shown below.

$$3SiO_2 + 4Al \rightarrow 3Si + 2Al_2O_3 \quad (\Delta H = -712kJ) \qquad \text{(fron Ref.126).}$$

Al-Si foundry alloys are particularly susceptible to corundum formation due to their already appreciable silicon levels. Corundum formation in these alloys has been investigated by Neff and Teller[126], who found that the problem can largely be eliminated by the use of non-wetting alumina castable refractories and low silicon refractory bricks.

The Effects of Inclusions

It is very difficult to quantitatively state the effects of inclusions; to date no truly accepted means of measuring actual inclusion levels has been established (see below). Inclusions have been shown to: act as nucleating mediums for porosity, decrease fluidity, promote poor surface finish, act as voids and cracks within castings, cause rapid tool wear during machining and consequently cause higher down stream production costs and increased

rejection rates. Most literature on the subject of inclusions compares the properties of "clean" and "dirty" metal without quantifying the actual level of "dirt" present, hence large quantities of conclusive but only qualitative data now exists describing the consequences of increasing inclusion levels.

Recent work by Mohanty et al[127] has demonstrated a feasible method for the addition of controlled amounts of various inclusions directly to a melt, these methods involve injecting inclusions below the melt surface. This development will enable the behaviour of various individual or groups of inclusion types to be studied, something which has previously been difficult. While this method of establishing the actions and influences of various inclusions has yet to be fully exploited, results have been presented which indicate that TiC, SrO and $Sr(OH)_2$ are not stable within aluminium melts. This oppugns the conjecture[95] that SrO and $Sr(OH)_2$ enhance porosity in modified castings. Mohanty et al's[127] work has also suggested that TiB_2 particles do not assist in the nucleation of solid phase in an Al-Si alloy, however more data than that supplied is required to fully substantiate this proposition.

Since most inclusions are solid throughout the casting process they can greatly influence fluidity and hence mould filling. The measurement of alloy fluidity with any accuracy is difficult, hence the effects of inclusions on this property come from physical observations and cogent arguments rather than by physical measurement. Decreased fluidity effects surface finish by reducing mould penetration and theoretically producing smoother castings.

Inclusion levels can also influence finish by two other means. Firstly, if clean melts are obtained by additions which reduce melt surface tension (e.g. sulphur) it is conceivable that if this state persists during mould filling surface finish will worsen, particularly when sand moulds are employed. Secondly, as mould filling takes place, the melt surface oxide layer where inclusions congregate, sweeps past the mould wall and tends to become attached, so causing oxide films and other solid particulate from the surface to collect against the mould wall[128].

The variance in mechanical properties due to inclusions has been analysed in a slightly more quantitative manner, yet most published results are still difficult to use in any more

than a general way. Variations in mechanical properties by inclusions can be directly attributed to increased porosity and a lack of strength in the bonding between inclusions and the matrix they occur within. The film-like morphology of some large inclusions means that they act in a very similar way to cracks, including the associated high stress concentrations at their edges. Turbulence during mould filling or the meeting of metal from two low temperature sources within a mould can create "cold shuts". These provide extreme examples of the crack-like nature of oxide films and show how severely inclusions can limit mechanical properties.

Chiesta et al[129] carried out a study on the effectiveness of various filters by monitoring the variation in mechanical properties of filtered and unfiltered sand-cast Al-7Si-Mg. Woven glass, metallic grid, steel screen and ceramic foam filters were investigated, all of which noticeably improved the mechanical properties of the cast specimens. The results of this study are shown in Figure 18, which illustrates the effect of filtration on porosity and Drouzy et al's[44] quality index, as discussed in Section 2.2.2 ($Q(MPa) = TS(MPa) + 150\log_{10}Elongation(\%)$).

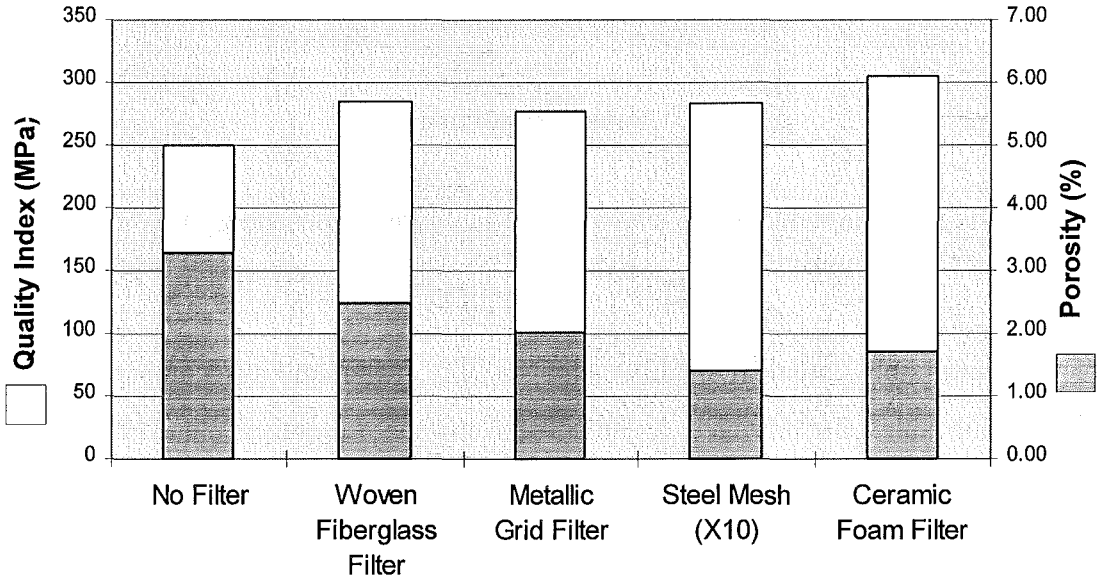


Figure 18: The ability of various filter mediums to improve cast quality (from Ref. 129)

A further study of the Al-7%Si-Mg alloy was carried out by Devaux et al[130] who cast and tensile-tested hundreds of filtered and unfiltered samples. The fracture surfaces of Devaux's[130] samples were examined and the samples rated according to the length of the

largest defect observed. The large number of tests carried out established that filtration removes the lowest strength samples from the scatter of tensile test results and can effectively reduce scatter by a factor of at least two, which corresponds to approximately ten times less rejections at specifically imposed minimum property values. For example, if 20% of unfiltered castings are rejected by a quality index criterion, filtration should reduce rejects to around 2%. Statistical analysis of the collected inclusion length data enabled Devaux to establish a relationship between defect length and variation in quality index; this relationship is shown in Figure 19.

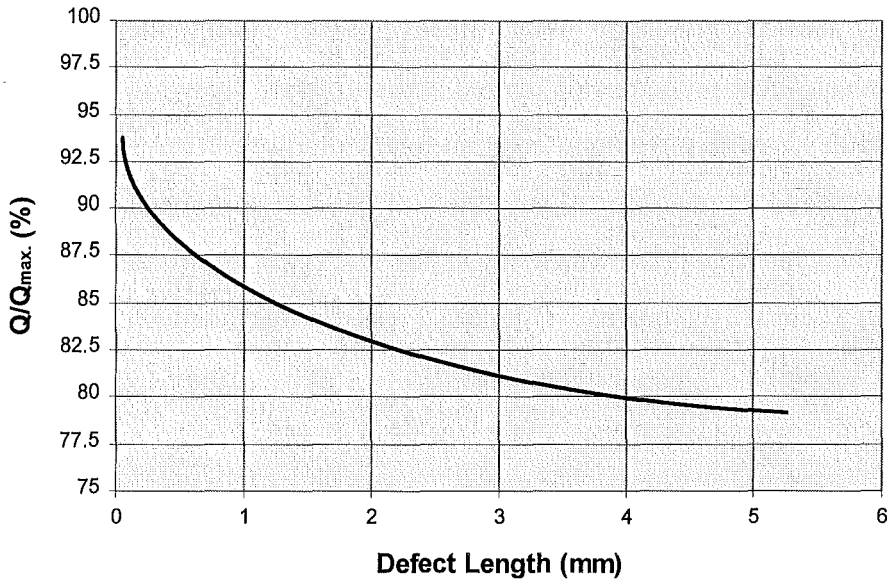


Figure 19: The reduction in average cast quality and consistency due to inclusions (from Ref. 130).

Figure 19 relates the statistical quality achieved (i.e. mean quality) compared to the maximum achievable. For instance, it can be seen that with a defect length of 4mm the average quality is only ≈80% of the maximum, whilst for a 0.5mm defect the mean quality is ≈90% of the maximum. The outcome of this is that, all things being equal (porosity, composition, etc), lowering inclusion levels and sizes greatly improves the consistency of cast pieces by raising the minimum quality achieved at any specified level of significance.

The influence of inclusions on fatigue properties was highlighted in the research by Wakefield[120], mentioned earlier. Wakefield constructed a furnace which allowed melting under an inert atmosphere, followed by degassing with nitrogen and direct tapping of metal slightly above the base of the melting crucible. This proved effective at reducing oxide and

inclusion levels to a minimum. One outcome from Wakefield's[120] work was that bottom tapped non-HIPed metal displayed higher minimum fatigue life, higher average fatigue life and less scatter than similar, conventionally-cast HIPed material.

One of the most significant effects of inclusions which has a direct influence on the cost of producing cast components is the phenomena of "hard spots". Hard spots consist of individual or clusters of inclusions which act as hard particulate within the alloy matrix. The extreme hardness of most inclusion particles results in rapid tool wear during machining and an associated difficulty in achieving good surface finishes. In the case of corundum particles, it is not unusual for cutting tool edges to be completely broken off, even when carbide tipped tools are used. As both machinability and inclusion levels are virtually unquantifiable at present the only information on this issue is from industry machine-shop observations. The financial significance of reduced tool wear is stressed in some reports[131] and is of particular relevance to machine-shops processing mass produced castings as they invariably utilise expensive dedicated cutting tools which can rapidly be reduced to scrap by inclusions.

2.5.2 Inclusion Removal

Inclusions may be removed by one of three mechanisms: filtration, sedimentation and entrapment within a dross upon the melt surface. The last of these mechanisms relies on direct extraction of particles as they meet the surface flux and dross via flotation or convection.

The beneficial action of various capping fluxes on inclusion extraction has been known for decades, however it is only recently that publications[132] have been available fully explaining these processes. Almost all available fluxes rely on the cleaning and capping action of chlorine and fluorine salts such as $BaCl_2$, KCl, NaCl, KF, etc. These salts are hygroscopic and accordingly, must be kept as dry as possible. Even in a well-dried state some of these salts may take over ten minutes before they stop oxidising the melt and actually strip oxides from the molten alloy surface. Sodium fluxing salts are not employed with alloys containing magnesium as this is accompanied by significant loss of magnesium even though the formation of NaCl is far more thermodynamically favourable than $MgCl_2$.

Flotation, which is greatly assisted by bubbles of purge gas, is obviously associated with degassing and hence it has been detailed above.

Except for the production of high conductivity aluminium and the re-refinement of certain scrap metal, sedimentation is not widely used as a method of inclusion extraction. When hexachloroethane is used as a degassing agent it is often recommended that a quiescent settling period of at least 15 minutes be allowed so that any silicon-carbide/aluminium carbide which may have formed has time to separate out. Some of the main inclusions which experience significant sedimentation are the borides which are deliberately added for grain refinement purposes. If coarse grain refining products are used pronounced sedimentation can occur during the quiescent period preceding casting. This is evidenced by the improved refinement which occurs if stirring is conducted immediately prior to casting.

Inclusions which are small or have similar density to aluminium tend to remain in suspension due to convection, thus these particles are not effectively removed by sedimentation. Accordingly, sedimentation is slow and only accounts for the removal of a small proportion of the typical inclusions present. Extended quiescent periods required for sedimentation are often detrimental to certain properties such as grain refinement and modification. By virtue of these facts, sedimentation is a secondary process which is seldom deliberately included in molten processing schedules. As noted above, the benefits of molten metal filtration are often substantial, however this process is dedicated to the removal of solid particulate from the liquid stream, and as such it cannot remove liquid inclusions such as $MgCl_2$. Filtration consists of passing molten aluminium through a porous device in which the inclusions present in the metal are retained by cake or depth filtration mechanisms. Filters must have sufficient strength, corrosion resistance, refractoriness and thermal shock resistance so that they withstand the molten metal environment and hence most filters are constructed from ceramic materials.

Depth filtration is a process whereby particles finer than the filter pore size are retained due to either direct interception, fluid dynamics or inertia sedimentation, as illustrated in Figure 20.

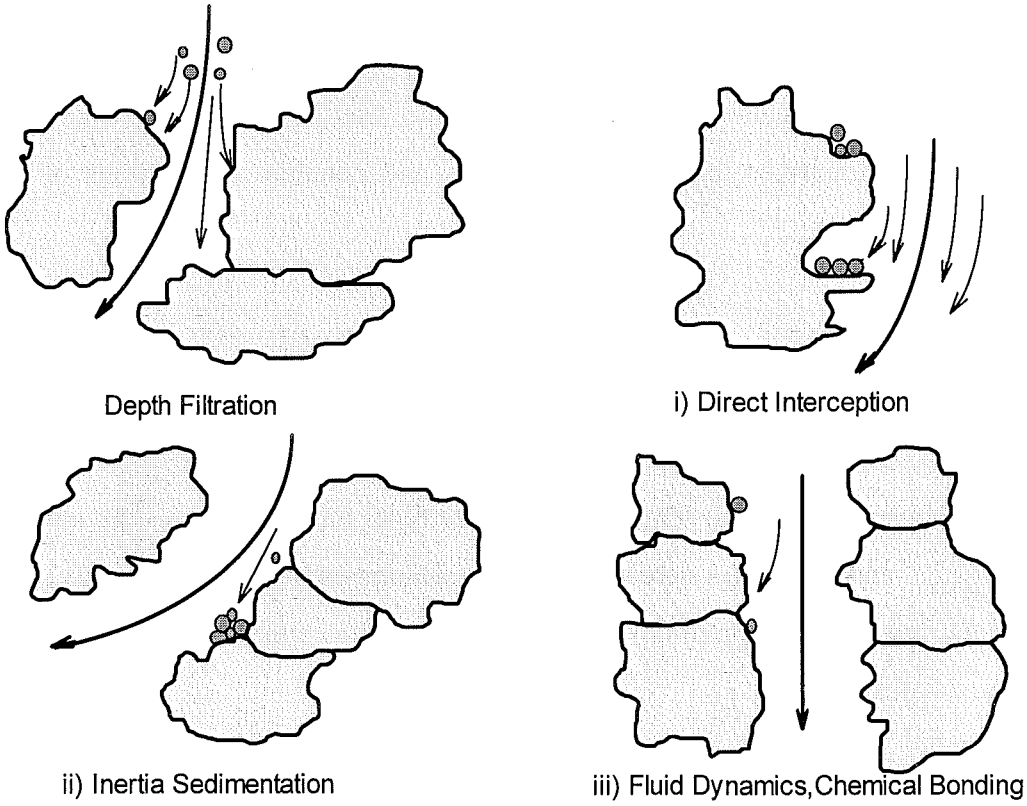


Figure 20: The main mechanisms by which depth filtration occurs

As is obvious, this process becomes more effective when filtering mediums are chosen that have rough surfaces and complex flow paths. Once contact and initial particle retention is achieved the particles may be retained by one or more of the following means:

- Gravity filtration
- Chemical bonds
- Electrostatic forces
- Physical entrapment
- Van der Waal's forces.

Ceramic foam and particle filters lend themselves to depth filtration, however their effectiveness is complicated by the varying capabilities of different ceramic surfaces and compositions.

Cake filtration involves physical entrapment of inclusions on the filter surface so building up a constricting "cake" layer. As the pores in the "cake" are substantially smaller than those of the filter which they partially obstruct, finer particles than might otherwise be

expected are removed from the melt. The effectiveness of cake filtration is dependent on the cake depth and permeability and hence varies with time. Compromise must be reached between melt flow rates, cleaning effectiveness and filter life. Back-flushing (where possible) to dislodge accumulated cake goes some way to alleviating cake build-up problems and so improves the cost effectiveness and potential applications of filtered metal.

Filter Types

Several filter types exist with ceramic foam filters being by far the most common. The less common types include metal and fibreglass screens, ceramic cells, bonded particle boards, cartridge filters and bed filters. Each of these filter types has its own specific advantages, however metal and fibreglass screens are now seldom employed. The only users of cartridge and bed filters are premium quality and large scale industries, hence these devices will not be detailed here.

Due to the versatility and effectiveness of ceramic foam filters they have become virtually an industry-wide standard. These filters have found widespread use in every area of alloy processing and are produced in forms ranging from sampling discs less than 40mm in diameter to large incline screens of around $1000cm^2$ as used in the primary aluminium industry. Although ceramic filters are not cheap, they may be used several times, are reliable and effective and utilise both depth and cake filtration mechanisms. On an out-of-mould basis only large bed filters, which are used in high volume situations, can provide better effectiveness and cost per unit metal filtered. Foam filters are available in a number of pore sizes ranging from 5 pores per lineal inch (PPI) to 30 PPI. Filters of around 20 PPI are most often used as it has been experimentally[130] determined that when foams finer than 20 PPI are used the area of filter required for useful flow rates rapidly increases to impractical proportions.

Ceramic filters of a cellular nature have been used and investigated. However, since they offer no real advantages over the more common foams they have not found widespread use.

Early attempts to filter molten aluminium included the use of metal and fibreglass screens. However, these processes have now been replaced by the use of ceramic foams. Although conceivably only filtering out the largest inclusions, screens have been shown by Chiesa and Raymond[129] to be effective at reducing the porosity and improving the quality (as defined by the quality index mentioned above) of cast samples. Chiesa and Raymond's[129] practical results comparing woven fibre glass, metallic grid, steel screen and ceramic foam filters led them to the conclusion that cheap woven fibre and metallic grid filters are only slightly less effective than ceramic foams. Whilst not conducting a full statistical analysis these authors suggest that the use of foam type filters may not be economically justified for the production of non-premium quality castings.

Bonded particle filters consist of refractory grains of Al_2O_3 or SiC bonded together to form a rigid mass. These filters are far more dense than ceramic foams and act more effectively in the depth mode of inclusion removal. Although bonded particle filters may be back flushed, they require large surface areas for given flow rates so their use is limited to mainly in-furnace applications.

Filter Positioning

Filtration may be carried out whenever molten metal is transported from one region to another. Consequently, filtering mechanisms have been developed which range from within the melt crucible to immediately prior to metal entry into the final casting cavity.

In-furnace filtration can be carried out by partially immersing porous vessels which have filters attached to their periphery, so that clean metal may be removed from the vessel centre. Alternatively, filter baffles may be fixed between charging and metal extraction regions. Both of these methods may be employed within large dip-out well or crucible furnaces. The latter method may also be used to filter metal within transfer ladles or melting crucibles of quite moderate size. Publications by Groteke have outlined the methods and applications of in-furnace[134] and point-of-pour[131] filters. In large operations where metal is processed, "in-line" filters may be extremely complex and integrated with degassing operations, or simply consist of single replaceable ceramic foam filter elements which are usually mounted in a horizontal position.

Outside large primary industry installations, the incorporation of filters into mould gates and runners was one of the earliest successful methods of introducing filtration to commercial foundries. In-mould filtration is possibly the most common form of filter placement, almost always employing ceramic foam filters. Although it seems logical to filter metal in the mould (i.e. at the last possible step), the need to fill moulds at an acceptably fast rate requires in-mould filters to be more open and less effective than filters used earlier in the processing cycle. In the past in-mould filter installations have simply been built into existing runner and gate layouts and it is only in the last few years that companies have designed moulds to exploit the reduced turbulence and flow inconsistencies which occur in post-filter flow streams. Complex in-gates can sometimes be completely replaced by direct pouring into the mould cavity via filter-containing insulating sleeves. This more holistic approach to filtered mould design has been successfully employed industrially, significantly reducing mould complexity and increasing cast yield. Commercial insulating sleeve and filter units are now available; for example Foseco market a unit under the DYPUR™ name. Information published by Sandford[135] regarding the direct pour process claims improved yield, lower pouring temperatures, enhanced directional solidification, less shrinkage and less felting than is encountered using conventional gate filtration practices.

2.5.3 Inclusion Monitoring Methods

Assessing melt cleanliness in a quantitative way has proven extremely difficult. Of the known methods, rapid and cheap techniques are qualitative at best, and more sophisticated quantitative tests are non-definitive and usually prohibitively expensive.

Inclusion measurement is complicated by the desire to ascertain the inclusion concentration and the frequency at which various inclusion sizes occur. Current techniques used to monitor inclusion levels may be separated into the following groups:

- Shop floor tests
- Chemical analysis
- Quantitative volumetric tests
- Metallographic techniques
- Non-destructive (molten metal) analysis.

The ultimate aim of any inclusion monitoring system is to assist in the elimination of initial particulate formation within the melt, so minimising the need for downstream processing and assuring that final castings are as defect-free as possible. Inclusions are added directly to the melt in the form of procured processing agents and in-house scrap; they are also continually generated by chemical reactions (oxidation, etc) and physical entrainment (refractory particles, etc). Hence, for the foreseeable future inclusion contamination of foundry melts is unavoidable. Resigned to the inevitability of inclusions, processes are required which rapidly assess melt cleanliness so obviating possible casting and processing of substandard material. To date this aim has not been fully realised as current shop floor processes include visual observation of fracture surfaces and Straube-Pfeiffer type vacuum tests, neither of which produce any more than qualitative data.

Chemical analysis by methods ranging from emission spectroscopy to gas chromatography can be used to quantify inclusion contents via the levels of various elements and compounds within a melt. These processes are beyond the practical scope of most foundries and usually require more time than is available if the results are to be of use prior to melt casting. The other major limitations with these methods of analysis are that they do not reveal the distribution of inclusion sizes present, or distinguish between the forms in which various elements are encountered.

Volumetric inclusion analysis involves taking a set size melt sample, then concentrating the inclusions into a specific region so their volume can be ascertained. Alcan and Union Carbide have developed similar processes based on this idea known as PoDFA (Porous Disc Filtration Apparatus) and LAIS[123]. These systems involve passing a set amount of molten metal through a foam filter, then sectioning the filter so as to determine the cake depth per unit of metal filtered. This process has proven to be effective, however it does not take account of very small particles and requires time for metallographic preparation and examination of the filter disc. Centrifugal inclusion separation, and monitoring the time for a set amount of metal to pass through a filter are other methods used to quantify melt cleanliness, however these have not proven to be suitable for commercial use. The most advanced volumetric analysis technique involves melting a sample under vacuum with an electron beam and then monitoring the inclusions which collect on the sample

surface. The high inherent cost and need for skilled personnel to carry out this form of analysis means it is useful for research purposes only.

Image analysis can be used to detect inclusions in metallographically prepared samples by colour variation between the inclusions and the matrix. This method of analysis has the advantage that it can provide data on inclusion counts and size distributions. Apart from protracted sample preparation, the major problems with this process include obtaining a truly representative sample and clearly differentiating between eutectic silicon and inclusions within foundry alloys.

Two on-line molten metal analysis techniques have been developed; one is based on a process very similar to the Coulter Counter, while the second uses a pulse-echo ultrasonic technique. Both of these techniques have been employed industrially although interest in the latter has declined as its limitations are realised. Reynolds Metals has developed equipment based on ultrasonic analysis, however this equipment can only detect inclusions greater than 60μm in size and does not provide information on particle size distributions. The Coulter principle involves passing metal through a narrow aperture over which a high current is passed. When an inclusion passes through the aperture a voltage pulse is recorded. The particle quantity and size distribution can be determined by the pulse distribution and particles down to 5μm can be measured. Alcan has developed hardware to monitor inclusions by this technique which is marketed under the LIMCA title. Apelian has briefly summarised the LIMCA test twice; once in 1989[121] when its accuracy and reliability was said to be questioned, and then again in 1992[122] when no mention of its accuracy and reliability was made.

Provided the accuracy and reliability problems have been resolved the Coulter method appears to be the most promising quantitative method of inclusion analysis. Its application is limited by the high equipment cost and the on-line nature of current designs. In smaller foundry environments only qualitative analysis techniques are currently feasible, with vacuum (Straube-Pfeiffer) tests in conjunction with separate hydrogen analysis (Alscan, Telegas) being the most informative.

All of the above melt cleanliness monitoring methods have been dealt with in publications by Gruzleski[18P] and Apelian[121,122].

2.6 THE EFFECTS OF IMPURITIES AND ALLOYS

2.6.1 Quantitative and Qualitative Results

Three major problems are encountered when attempts are made to quantify the effects of various elements in aluminium alloys. Firstly, several elements interact, which means that their individual effects may not be consistent with their effects when other elements are present. Secondly, numerous alloy processing procedures exist and even slight changes in these processes can drastically change the influence of various elements. Finally, the wide range of alloys and impurities commonly encountered means that only a limited range of elements can ever be investigated. These factors lead to the inevitable variability associated with commercial castings and dictate that limited quantitative results must result even from extensive testing and must be presented in a statistical manner.

When it is realised that statistical results can only be used in the context from which they were gained, the very limited scope of application for most published data becomes evident. A consequence of the factors listed above is that most published results are qualitative without any indication of physical magnitude and tend to centre around specific alloys and sets of added elements. These facts lead to summaries of element effects which are necessarily vague, imprecise and conservative ... and hence of marginal real use.

Published Qualitative Data

Although almost all articles and texts concerning aluminium castings make some qualitative statements on the effects of various elements, two of the most comprehensive summaries are contained within the ASM, "Aluminum and Aluminum Alloys" specialty handbook[133] and Mondolfo's classic text, "Aluminium Alloys - Structure and Properties".[78A] These two texts summarise the results of hundreds of investigations. Mondolfo's book[78A], published some 20 years ago, quotes 385 references on Al-Si and Al-Si-Mg alloys alone (a field which has been the subject of extensive research and development since that time). Possibly the most useful aspect of Mondolfo's work is that it serves as an excellent guide from which to obtain references for any specific area of interest. The ASM text[133] is not as detailed in its comments and does not guide the reader toward articles of relevance for more detailed information. It does, however, have the advantage of being more up-to-date and concentrates only on issues of relevance to foundry-related products.

Other sources of data regarding the actions and interactions of various elements can be gained from foundry product manufacturers in the form of instruction manuals, data sheets and information packs. Whilst of a commercial nature, these publications often stem from extensive research carried out by research organisations affiliated to the various companies and meet the needs of both the customer and the parent company throughout the aluminium industry.

Published Quantitative Data

Published quantitative data is usually presented in the form of graphs complete with trend lines. Unfortunately, these plots often stem from scant physical data and make little or no allowance for experimental scatter. Often such plots are purely based on conjecture. Irrespective of the form in which experimental results are presented or reproduced, the original source of experimental results must be consulted, so that the potential variability due to the numerous alloy processing parameters available may be assessed prior to acting on, or accepting, the results in question. A further problem arises with the Al-Si eutectic alloy as most foundry-based data, particularly recent work using modern processing methods, centres on the Al-7%Si-Mg alloy which, while similar, is quite different in nature.

The properties of the eutectic alloy are dominated by the silicon level and the morphology in which silicon is present, i.e. modification. The addition of more than ≈0.1% magnesium in Al-Si-Mg alloys virtually eliminates the effects of silicon variation and silicon morphology is far less significant due to reduced volumes of eutectic phase. The differences between the Al-7%Si-Mg and Al-Si eutectic alloys are compounded by the fact that the former is commonly used and researched in the permanent-mould / heat-treated state, while the latter tends to be sand-cast and does not respond to heat treatment. Vicariously applying quantitative results from research on the Al-7%Si-Mg alloy to Al-Si eutectic products is clearly inappropriate, so much so that even generalised qualitative comments may not apply to each of these seemingly similar alloys.

Research has taken place in Russia aimed specifically at establishing the quantitative effects of compositional variation on the mechanical properties of alloys of the Al-Si-Cu-Mg-Zn type. This research, centred on secondary alloys, has included alloys which fall

very close to, or within the bounds of the BS-1490-LM6 standard. Work by Berezyanskaya et al[136] published in 1983 varied and monitored the content of six elements (Si, Cu, Mg, Fe, Mn, Zn) at five levels each. The tensile and hardness properties were established in both the as-cast and heat-treated states and the resultant data was analysed using a form of multi-linear-regression (MLR). As MLR allows several variables to be adjusted at once, Berezyanskaya et al[136] minimised the number of required cast specimens using experimental design matrices. These researchers failed to realise that reducing the number of samples assumes that little or no significant variation may be present due to factors beyond those monitored and included as control factors. Variations due to processing parameters, metal cleanliness, property measurement, etc are known to be significant for all cast alloys, hence the properties of any single composition can only be established on a statistical basis. The need to counteract unavoidable casting variance via increased sampling necessitates the use of large numbers of test pieces, particularly when several factors are being investigated simultaneously. As Berezyanskaya varied six elements yet indicates monitoring of only 32 samples, the analysed results can only be credited with minimal significance. The MLR method employed is also open to question as very few variable permutations seem to have been tried and no optimisation or removal of insignificant factors seems to have taken place. It can only be concluded that the above work yielded unusable results.

Work by Bychkov et al[137] in 1986 investigated the same elements in a similar alloy by the same process as Berezyanskaya et al[136]. In this case over 500 observations were made, which is sufficient provided control was exercised over all sources of variations other than the composition. This work seems to have been analysed with little regard for the limitations of MLR. Once again, very few predictor factors seem to have been trialed and the resulting equations do not seem to have been optimised in any way. The cavalier attitude given to this MLR analysis is demonstrated by an expression for tensile strength which includes 11 individual factors yet has a Fisher criterion* of 1.24. This low Fisher value indicates a reasonable possibility that the predictive worth of the entire equation is nil and that some of the included variables certainly have no significant worth. The outcome of this is that the results of this research cannot be regarded as useful in any way.

* Detailed in Section 7.2.

Several references which have made quantitative remarks regarding the Al-Si eutectic alloy are included in the following section. These results have not been generated from MLR analysis, rather they have been obtained from adjusting one variable at a time and plotting the results.

2.6.2 The Effects of Elements Directly Relevant to this Research

SILICON - While Kashyap et al[138] suggest that in the 4-12% range, silicon has negligible effect on mechanical properties, closer examination of the data from which this observation is made[139] shows that the above is only true with Mg levels over ≈0.1%. At low Mg levels, the effects of silicon can be predicted from comments by authors such as Harris et al[139] and Charbonnier et al[140] as being:

- Tensile and yield strength are optimised between 10 and 12%Si with increases possibly being as high as 25% and 80% respectively compared to an Al-4Si alloy.
- Ductility decreases steadily as silicon levels rise from over 10% elongation with 4%Si to below 3% with 13%Si.
- The major influence of silicon is to improve castability via improved fluidity, reduced shrinkage and less tendency for hot tearing.

Silicon forms compounds with Fe, Mg, Mn, Ti, Cu and Zn, however the latter three are not encountered in alloys within the BS-1490-LM6 standard.

MAGNESIUM - Magnesium is added intentionally to some Al-Si eutectic alloys subject to fatigue (such as road wheels), however these additions are usually at levels beyond that permitted (0.1%) by BS-1490-LM6. Experimental results from Charbonnier et al[140] are presented in Figure 21.

This work suggests that, compared with magnesium's absence, 0.1%Mg has the following effects:

- Tensile and yield strengths are increased by 10 MPa.
- Ductility is reduced from 10 to ≈7% elongation.
- Fatigue strength is improved by up to 15 MPa (30%).
- Impact strength is approximately halved.

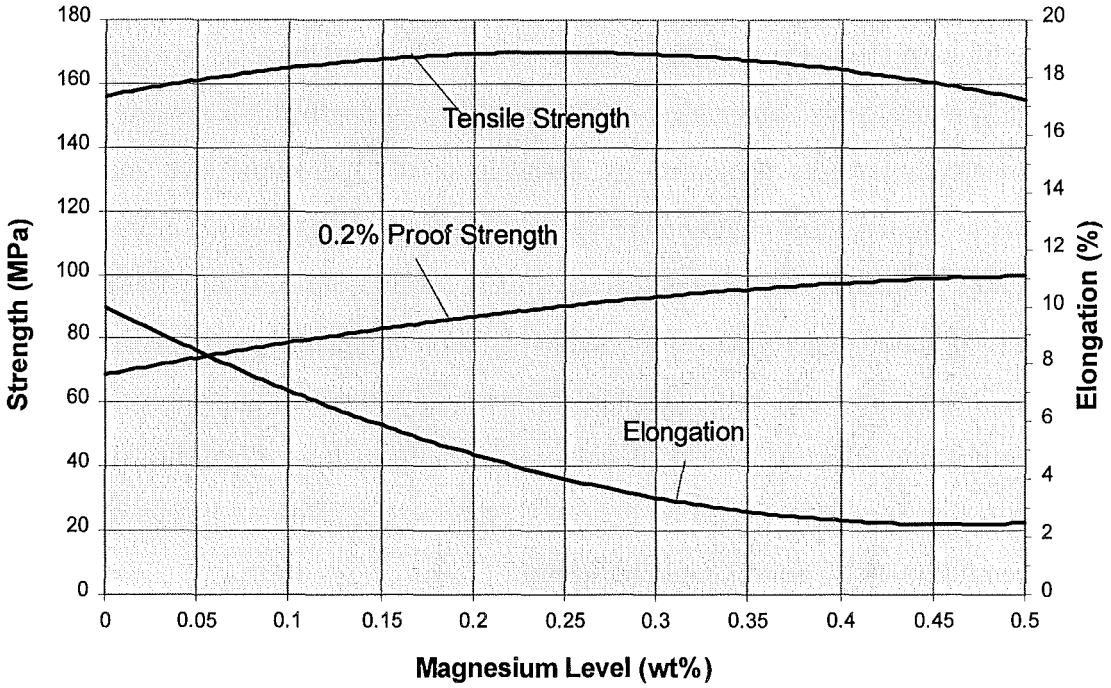


Figure 21: The effect of magnesium on Al-11%Si alloy (from Ref. 140).

As mentioned above, magnesium may prove highly detrimental to casting properties if associated inclusions such as spinel are permitted into the melt. Magnesium is known to form Mg_2Si when Fe% < Mg% and $FeMg_3Si_6Al_8$ when Fe% > Mg%. The second of these situations is almost always the case with foundry alloys of the BS-1490-LM6 type. Research at Aluminium Pechiney[34] has also shown that magnesium causes eutectic coarsening, however this should be minor when magnesium levels are held below 0.1%.

IRON - Iron is one of the main impurities found in cast alloys and is associated with large decreases in ductility, thus iron levels are minimised wherever possible. Data is available regarding the Al-7%Si-Mg alloys which show that iron is detrimental to <u>all</u> tensile test properties as well as fatigue[141,113]. Comments in the ASM handbook[133B] and Mondolfo's[78B] text mentioned above suggest that iron may increase strength, whilst being detrimental to ductility, at least until primary $FeSiAl_5$ begins to form at iron levels beyond ≈0.7%. Iron has the benefit of reducing die sticking and soldering in permanent moulds. It also reduces hot tearing but is detrimental to casting characteristics due to the formation of several insoluble compounds with elements such as manganese and magnesium.

MANGANESE - Manganese is not added intentionally to virgin casting alloys. It is, however, often present in secondary metal produced from recycled wrought product. Mondolfo[78B] indicates that manganese slightly increases strength at the expense of ductility whilst conversely, results presented by Kashyap et al[138] illustrate that manganese is detrimental to the tensile strength of the Al-7Si-Mg alloy. A 1989 study at the University of Canterbury[26] which aimed to establish the effects of additions of 0 to 0.5%Mn on virgin sand-cast LM6 failed to detect any attributable variation in mechanical properties.

Manganese has traditionally been added to secondary alloys containing appreciable iron so that the embrittling effect of $FeSiAl_5$ is reduced by the formation of $(FeMn)_3Si_2Al_{15}$. This corrective action is recommended by Foseco[46], who suggest addition levels related to the iron concentration by the following relationship:

$$Mn\% = 2 \times (Fe\% - 0.5).$$

It is pointed out by Mondolfo[78C] that excess manganese is not conducive to good cast characteristics as $(FeMn)_3Si_2Al_{15}$, which forms as primary crystals when $Fe\% + Mn\% > 0.8\%$, does not embrittle castings but substantially reduces machinability. Results presented by Kashyap et al[138] show manganese as having a marginal-to-nil beneficial influence on the tensile strength of Al-7%Si-Mg alloy containing iron at levels from 0 to 1%. Their results actually show manganese as detrimental until iron levels exceed 0.45%. Ductility values, which are not provided, may have shown manganese in a more positive light. It is interesting to note that the ASM Handbook[133] makes no note of the iron-corrective nature of manganese; it is simply mentioned that insoluble phases such as $(FeMn)_3Si_3Al_{15}$ are detrimental to feeding and flowability.

As both sodium and strontium cause modification the comments in Section 2.2 regarding the effects of modification may be related to the following two elements.

SODIUM - The silicon-modifying action of sodium has been mentioned earlier, as has the unstable nature of its presence within molten aluminium. As expected, the physical effects of eutectic silicon refinement are most pronounced in alloys close to the eutectic composition such as BS-1490-LM6. Foseco[46] has published a chart, shown in Figure 22, that quantifies the effects of sodium. However, no indication is given as to the source of this data, or to the alloy and casting conditions to which it relates. The large indicated effect due to modification would suggest that the alloy in question is sand-cast and of the

Al-Si eutectic type. Given that modification has been subject to extensive research since its introduction in the 1920s it is surprising to note how little quantitative data exists on the topic. ASM[133B] credit sodium as being detrimental to ductility in alloys containing magnesium, although no reason is given as to why this should occur with sodium and not strontium.

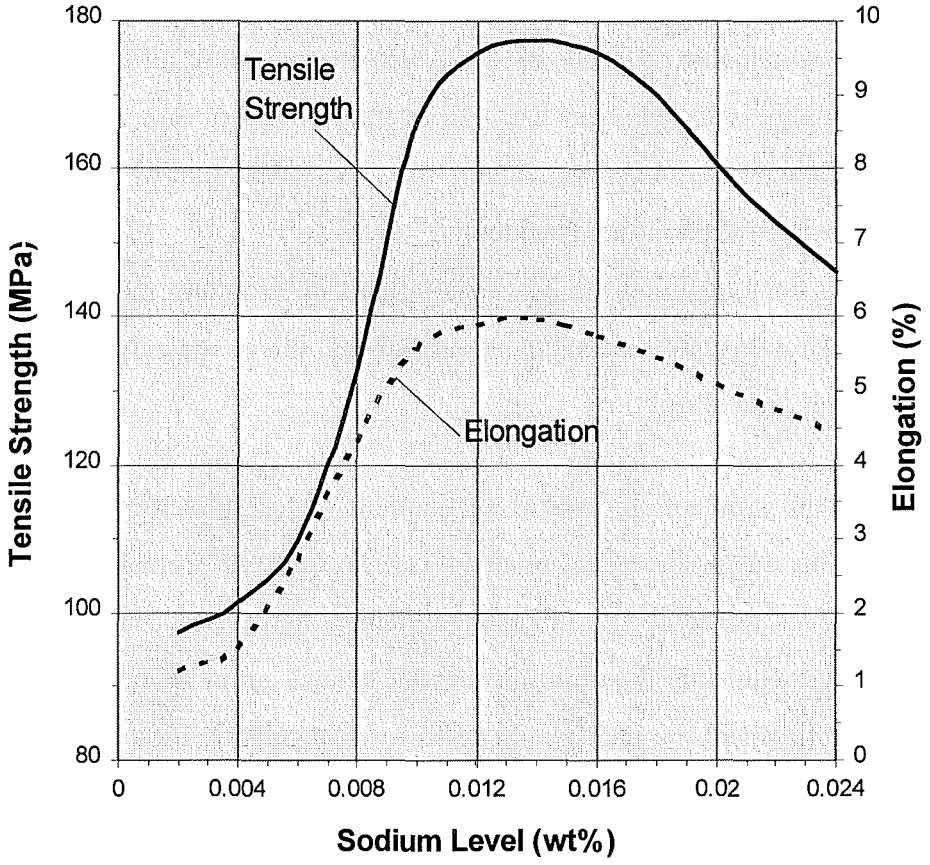


Figure 22: The tensile effects of sodium (from Ref. 46).

Excessive sodium causes very thick oxide layers to rapidly form on melt surfaces which hinders castability and increases the likelihood of large inclusions being encased into cast surfaces. As discussed in Section 2.4, sodium is often associated with increased porosity; this is also true when additions to the melt are carefully controlled. If sodium levels exceed ≈ 0.01% $(NaAl)Si_2$ may form: this phase promotes silicon nucleation and causes the coarsening of some silicon particles[18Q,78D].

STRONTIUM - As strontium produces less uniform modification than sodium, it can be expected that the property improvements will not be of the same magnitude, particularly in alloys predominantly eutectic in structure. Strontium modification is often stated as being insensitive to overmodification[29,142A]. This comment must come from the observation that overmodified structures, such as those obtained with excessive sodium, do not form with excess strontium. From a property point of view, excess strontium can be highly detrimental. Gruzleski[18R] acknowledges the detrimental effects of excess strontium as does Kawecki-Billiton Metaalindustrie (KBM) in an Al-Sr master alloy product guide[29]. However this KBM guide[29] also lists sensitivity to overmodification with Sr as "none", which is in direct contradiction to a later comment in the same publication which states that ductility is reduced if excessive strontium is added!
Quantitative data exists demonstrating the beneficial effects of strontium modification on the Al-7Si-Mg alloy. However, for reasons mentioned above, this is unlikely to be of any relevance to the Al-Si eutectic alloy.

TITANIUM - The potent grain refining nature of titanium was discussed in Section 2.3. Section 2.3 also contains quantitative data relating both (a) the time from alloy addition and (b) the titanium level, to the degree of grain refinement achieved. Titanium, in the form of Al_3Ti dissolves with time thus diminishing the related grain refinement. Apart from a lack of grain refinement, no data would seem to exist relating dissolved titanium levels to physical properties. Undissolved titanium levels can be related directly to grain refinement results provided the samples used experience the same titanium exposure period. As was mentioned in Section 2.3.6 grain refinement is reported as having an insignificant, or weak positive influence on the mechanical properties of Al-Si casting alloys[78E,27D]. Data shown within ASM texts[133C] show minor positive effects of grain refinement on the mechanical properties of an Al-7Si-Mg alloy, with the beneficial effects on ductility being significantly enhanced when modification is also carried out. Gruzleski[185] indicates that grain refinement (and hence titanium), is also beneficial to hot tearing and porosity distribution. Smith et al[119] report that as silicon levels rise, grain refinement decreases becoming negligible near the eutectic composition, so it can be assumed that the above minor positive effects will be minimised in eutectic type alloys.

BORON - Like titanium, boron grain refinement is covered in Section 2.3.6. Similarly to titanium, no direct quantitative data relating boron levels to physical properties (other than

grain refinement) has been found. It can be assumed that the beneficial effects of titanium grain refinement apply equally well to boron, albeit the same degree of refinement can be achieved at lower boron levels.

Boron is sometimes associated with harmful boride inclusions introduced via grain refining additives and the formation of sedimenting sludges, both of which drastically reduce final casting integrity. The potential thus exists for boron to be deleterious (via inclusion introduction) and advantageous (by refinement) at the same time.

COPPER and ZINC - These two elements are commonly added to foundry alloys because, subsequent to heat treatment, they significantly increase strength. Each of these elements may be added at levels as high as 3.0-5.0% in common wrought and foundry alloys, hence they tend to enter the foundry scrap cycle at reasonably high levels. Only 0.1% of each of these elements is permitted by the BS-1490-LM6 standard, so it is possible that either or both of these elements may be present up to the allowable limit in secondary alloy. BS-1490-LM20 (AA413.1) is virtually identical to LM6 except that copper is tolerated up to 0.4%; this alloy is reported[143] to have very similar strength but reduced ductility compared to LM6. By virtue of this, it is predicted that within the LM6 range copper will not cause an appreciable change in strength but may reduce ductility by a small amount (< 1% elongation).

Zinc is added to casting alloys in conjunction with either copper or magnesium therefore zinc is not usually found without one of these elements also being present. Other casting alloys which contain zinc and copper or zinc and magnesium are LM24 and LM2 (AA330), unfortunately these alloys vary so much from LM6 that they can not be used for comparative purposes. Mondolfo[78C] indicates that zinc up to 2.0% has no substantial effects on the room temperature properties of cast Al-Si alloys. From this it may be assumed that zinc causes no variation in properties of alloys within the BS-1490-LM6 composition range.

TABLE 3: Phases Formed in Eutectic Al-Si Alloys

(From Mondolfo[78A], Closset & Gruzleski[18], Ref[144] and Handiak[33])

Si	Si < 12% eutectic	Si > 12% primary & eutectic	Fe > 0.05% $FeSiAl_5$	Mn > 0.1% $(FeMn)_3Si_2Al_{15}$	Fe > Mg $FeMg_3Si_6Al_8$	Mg > 2Cu $Cu_2Mg_8Si_6Al_5$
Fe	Fe < 0.7% eutectic $FeSiAl_5$	Fe > 0.7% primary $FeSiAl_5$	Mn > 0.2% $(FeMn)_3Si_2Al_{15}$	Fe > Mg $FeMg_3Si_6Al_8$		
Mn	Fe > Mn $(FeMn)_3Si_2Al_{15}$	Mn > Fe $Mn_3Si_2Al_{15}$ + $(FeMn)_3Si_2Al_{15}$				
Mg	Mg < 0.2% in solid solution	Fe > Mg $FeMg_3Si_6Al_8$				
Ti	Ti < 0.15% $TiAl_3$ (dissolves)	Ti > 0.15% $TiAl_3$ + Ti in solution				
B	AlB_2 / AlB_{12}					
Na	Na < 0.01 Dispersed	Na > 0.01 $(NaAl)Si_2$	with Sb Na_3Sb			
Sr	with overmodification (0.01 + %Sr) Al_2Si_2Sr and Al_4SrSi_2		with Sb + Mg Mg_2Sb_2Sr			
P*	Si < 12% dispersed AlP	with Na dissolved in $NaSi_2$ or reacted directly Na to form Na_3P	with Sr dissolved in an AlSiSr type compound or reacted directly with Sr			
Cu	Cu < 1% in solid solution					
Zn	In solid solution					

* Detailed in Section 2.7

2.7 THE EFFECTS OF PHOSPHORUS

Phosphorus usually enters aluminium via contact with refractories, tools and crucible glazes, and is often present in virgin alloy at around 4-5ppm and at ever higher levels following subsequent processing.

Phosphorus acts on Aluminium-Silicon alloys in two distinct ways. Firstly, it promotes the nucleation of primary silicon in hypereutectic compositions and secondly, it coarsens eutectic silicon promoting lamellar and acicular structures. In both hypo- and hypereutectic alloys these effects are inimical to effective modification. To compound matters the minute amounts of phosphorus normally present (<10ppm) have incommensurately large effects on all cast properties.

As mentioned earlier (Section 2.2.2), the ability of phosphorus to assist the nucleation of silicon via AlP nuclei is utilised in hypereutectic alloys to increase the number of silicon nucleation sites and thus promote smaller, more uniformly dispersed primary silicon crystals. Refined primary silicon is conducive to improved melt fluidity and final casting ductility and wear characteristics. The most significant aspect of this practice is that it represents a large potential source of phosphorus in secondary alloy. As complete removal of phosphorus is not feasible, the only way to ascertain the phosphorus level present in primary or secondary alloy is to carry out compositional analysis; unfortunately analysis for phosphorus is far from routine.

Bercovici[34] at Pechiney has shown that the eutectic coarsening observed with increasing phosphorus levels is not caused by primary silicon crystals changing the eutectic silicon growth conditions by acting seed material. Bercovici[34] also reported results of the interactions between phosphorus and sodium, and phosphorus and strontium, on the eutectic structure of Al-Si eutectic and Al-7%Si-Mg alloys. The results of this study are shown in Figures 23 and 24. Bercovici also provides microstructures which clearly indicate that magnesium affects the eutectic in a similar manner to phosphorus but to a far lesser extent.

As can be seen from Bercovici's[34] graphical results, increasing the phosphorus level from 5 to 8ppm can more than double the amount of modifier required to achieve a similar degree of

eutectic refinement. This corresponds exactly to the range over which phosphorus is commonly encountered. By virtue of these facts and the lack of provision for phosphorus analysis with purchased foundry ingot, it is impossible for foundries to obviate the effects of the resulting modification variation by prior adjustment of modifier addition levels. Gruzleski[18T] notes the significance of these issues and suggests that the varying modification response of North American alloys from batch to batch may well be due to inconsistencies in phosphorus levels. The importance of this soon manifests itself when it is realised that if a requirement for 50% more modifier than is generally required, goes unnoticed 10-13%Si alloys can lose well in excess of 10 MPa tensile strength (from Fig. 22 in Section 2.6.2).

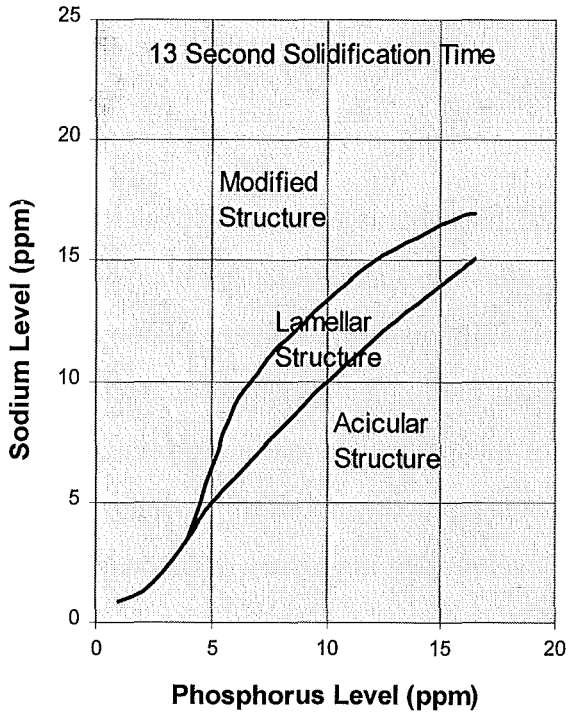


Figure 23: The interaction between sodium and phosphorus in Al-7%Si alloy (from Ref. 34).

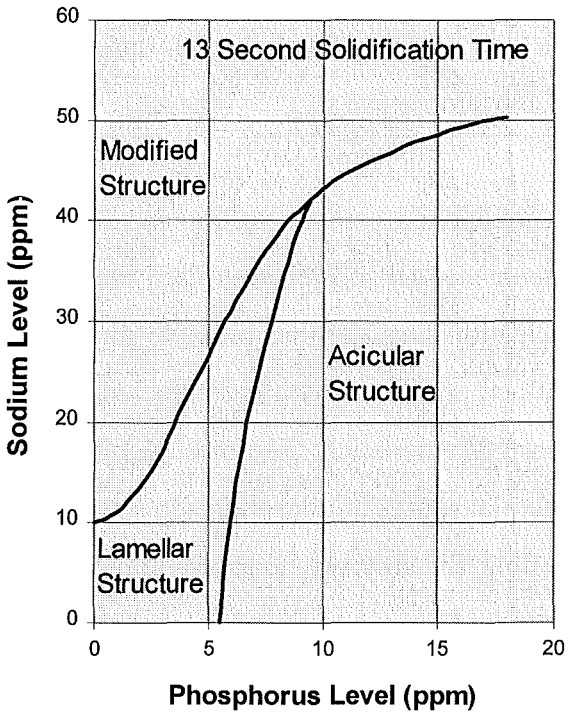


Figure 24: The interaction between sodium and phosphorus in Al-13%Si alloy (from Ref. 34).

Major and Rutter[7] have investigated the actual mechanisms by which phosphorus coarsens eutectic silicon. They observed that phosphorus progressively reduces the faceted nature of silicon whilst having exactly the opposite effect on the aluminium phase. Due to the very low levels of contaminant required to achieve this effect it was concluded that adsorption on the solid/liquid interface takes place by one of two mechanisms. Firstly, phosphorus may accumulate as a liquid species on the solid/liquid interface or, alternatively, phosphorus may

increase the total solid species present in the solidification monolayer by forming AlP at the solidification front. Support is given to the latter supposition as phosphorus has a very low solubility limit in aluminium.

Irrespective of the exact method of structural adjustment, phosphorus acts to poison modification. The growth restrictions on faceted silicon are eased and aluminium growth is retarded by making it more faceted in nature. This combination helps maintain the silicon as the leading solidification phase, thus suppressing the onset of modification.

The modifying agents, sodium and strontium, are thought to overcome these effects by forming compounds which react directly with, or dissolve phosphorus[18T]. The proposed compounds with sodium are $NaSi_2$ and Na_3P while those formed with strontium remain largely unknown.

All of the issues dealt with in the preceding literature review are covered in some detail in the following publications:

- "The treatment of liquid aluminium-silicon alloys", JE Gruzleski and BM Closset. AFS, Illinois, USA, 1990 (Ref. 18).
- "Aluminum and aluminum alloys", JE Davis, ASM International, Ohio, USA, 1994 (Ref. 133).
- "Aluminum alloys - structure and properties", LF Mondolfo, Butterworths, London, 1976 (Ref. 78).
- The Proceedings of the "International Conference on Molten Aluminium Processing" - 1986, 1989, 1992. AFS, Illinois, USA, 1986, 1989, 1992 (Refs. 145-147).

Most of the above references to the ASM "Aluminum and Aluminum Alloys"[133] handbook may also be found in the 9th edition of the "Metals Handbook" or "Casting", volume 15, ASM Handbook 1988, p743-770.

3.0 EXPERIMENTAL LAYOUT

3.1 PARAMETERS FOR INVESTIGATION

3.1.1 Compositional Parameters to be Examined

The proposed experimental procedure to quantify the effects of various elements and impurities in Al-Si eutectic foundry alloys consisted of the following sequence:

(a) Selecting the compositional variables and physical properties to be measured and producing an experimental design based on the following processes and their limitations;

(b) Producing a number of cast specimens varying in composition so as to represent the entire range permissible for the selected elements;

(c) Monitoring and quantifying the physical and chemical characteristics of the samples produced;

(d) Analysing the collated compositional and property results using statistical analysis via multi-linear-regression.

This chapter deals with the first of the above issues but is entirely dependent on the anticipated limitations of the latter processes and the financial and time constraints on the project.

Since the most common specification used within New Zealand when ordering Al-Si eutectic alloys is British Standard 1490-LM6 the composition limits laid out within this standard were used as the bounds for the present research (see Appendix A). The wide composition ranges permitted, particularly with regard to iron and manganese, allow secondary alloys to be produced which comply with this standard. The implications of this are that elements which are not found in virgin alloy (e.g. Mg) may be present at significant levels in LM6 produced from secondary metal.

One of the initial aims of this research was to quantify the effects of phosphorus on the mechanical properties of Al-Si eutectic foundry alloys. Phosphorus was considered worthy of investigation because, as was mentioned in Section 2.7, this element goes largely

unmonitored and the effect it has is incommensurate with the levels in which it is commonly encountered. The effects of phosphorus on the alloy structure are known, yet the changes in mechanical properties remain largely unquantified. Since phosphorus affects silicon modification the other elements known to play a part in this process, namely; Si, Na, Sb, Sr, Mg, Ba, Ca, etc were also regarded as significant for investigation. Of these, only Na, Sr and Mg are commonly encountered in locally processed alloys, hence these elements were regarded as the most preferable experimental variables. Since sodium is the most common Al-Si eutectic modifier, investigation into the effects of sodium are a prerequisite to studying the effects of phosphorus. Whilst it is not usual for strontium to be employed locally (NZ) as a modifier in eutectic alloys, there is no indication that it may not be used for this purpose in the future. It is thus conceivable that secondary metal originating from alloys such as Al-7%Si-Mg may contain significant levels of strontium and hence investigation into this element was also considered a necessity. As increasing volumes of imported alloy automobile wheels are recycled, antimony may play a more important role in local secondary alloys. At present antimony levels in New Zealand produced secondary aluminium is minimal and future contamination is not expected to reach high levels.

Iron is the major impurity encountered in virgin foundry alloys and, as mentioned in Section 2.6, is associated with detrimental effects on the physical properties, particularly ductility. The effects of iron are an issue of concern industry-wide, hence the use of 'correctives' such as manganese when iron levels exceed 0.3%. One of the investigations performed at the University of Canterbury[26] which concerned a foundry alloy of relevance to this research, aimed to determine if manganese was genuinely efficacious at improving the properties of high-iron alloys. The findings of this work were inconclusive, promoting speculation that iron is not as detrimental as commonly perceived and that correction via addition of elements such as manganese is of dubious benefit; clearly this issue deserved further investigation. It was hoped that including iron and manganese in the present research would provide a conclusive and quantified resolution of this matter.

Grain refinement of Al-Si casting alloys has become a standard procedure during molten metal processing; even so, the worth of refining these alloys is often questioned. Virtually

no decisive data exists revealing the magnitude of the influence that grain refinement has on final mechanical properties. Considering the common acceptance of the process, this lack of knowledge seems a rather large oversight. When the full complexity of grain refinement is realised the difficulty associated with assessing the usefulness of this process becomes obvious (see Section 2.3). As was also mentioned in Section 2.3, titanium, or titanium and boron in combination are virtually the only grain refiners of any commercial significance. Since the proposed research was to consist of monitoring and analysing numerous sample observations, it was hoped that grain refinement via either or both of these elements could also be successfully investigated.

The remaining elements permitted at potentially significant levels by BS1490-LM6 include: zinc, copper, lead and nickel. The effects of these elements were regarded as not being as deserving of investigation as those mentioned above for the reasons outlined below and discussed in Section 2.6. Reports that zinc has little influence on the room temperature properties of sand cast Al-Si alloys at levels up to 2%[78C] suggest that up to the 0.1% limit imposed by BS1490-LM6 the effects of zinc will be negligible and hence not worthy of investigation. It was thought unlikely that nickel or lead would be encountered at significant levels in secondary alloys; there also seems little reason for their deliberate addition. While nickel has been reported[78C] as an iron corrector in the same manner as manganese it is not usual for this element to be added for this purpose, mainly since manganese, is considered to have superior effects. Since copper is added as a strengthening agent to several heat-treatable casting alloys, it is conceivable that this element may be found at appreciable levels in secondary alloy. BS1490-LM20 has the same nominal composition as BS1490-LM6 except for an allowance of up to 0.4% Cu. In the sand-cast, unheat-treated state, the physical properties of these alloys are little different (LM20 being slightly less ductile) suggesting that minimal property variance could be expected within the 0-0.1% Cu range prescribed by the LM6 standard. For this reason copper was considered to be of less importance than the main elements mentioned above.

The composition variables considered worthy of examination are listed below in order of decreasing merit:

- Sodium
- Phosphorus
- Strontium
- Magnesium
- Silicon
- Iron
- Manganese
- Titanium
- Boron
- Copper
- Zinc.

Time and resource limitations restricted the number of the above elements which could be investigated. As described in Section 3.2 copper and zinc were excluded from the final investigation set.

3.1.2 Physical and Structural Properties to be Examined

A casting process can only be deemed successful if the required mechanical and morphological properties are achieved. The approved procedure (by Standards eg LM6) to assess the resultant mechanical properties is to conduct tensile tests of samples machined from castings produced in standard moulds. The significant parameters from these tests are the tensile strength and ductility, and hence virtually any research that is to be of use in a commercial foundry incorporates reference to these properties. The physical and structural properties which influence, or can be used to assess, the mechanical characteristics include:

(a) Porosity (if gross);

(b) Grain size (influence subject of debate);

(c) Modification level;

(d) Hardness;

(e) Primary aluminium dendrite content and form;

(f) The presence of detrimental intermetallic constituents within the alloy structure;

(g) The presence of inclusions.

Quantitative monitoring of these parameters would allow the significance of each and their correlations to the melt composition, to be assessed. Since the proposed research involved casting samples into standard moulds of consistent thermal characteristics, dendrite form (i.e. arm spacing) was not expected to vary between samples and thus would not require monitoring and assessment. Due to the uniform molten processing and casting procedures to be used, monitoring of the amount of primary aluminium and form of intermetallic phases present was also considered unlikely to yield much more information than was available in the composition data alone. As discussed in Section 2.5, accurately monitoring inclusion levels is a complex matter. At the experimental design stage of the current research no appropriate method by which inclusion assessment could be made was envisaged and thus no allowance was made for inclusion monitoring either during molten processing or at a later stage.

Within the composition range of a given standard alloy, large scale morphological characteristics tend to be controlled by the casting process (e.g. pouring temperature, mould layout, etc) rather than the specific composition of the cast specimens. As a result of this, once an alloy is selected as appropriate for a specific application, difficulties such as mould filling and thermal contraction are generally resolved by redesign of the mould layout rather than variation in melt composition. On a smaller scale, porosity and surface finish are strongly influenced by compositional changes, particularly changes in the modifying and grain refining elements. A result of this is that it is becoming increasingly common for foundries to monitor porosity, grain size and modification levels as a means of optimising smaller scale morphological and aesthetic characteristics as well as the physical properties. The factors which are related to the morphological characteristics include:

(a) Porosity,

(b) Grain size,

(c) Modification level,

(d) Intermetallics,

(e) Inclusion level,

(f) Molten metal hydrogen level,

(g) Fluidity,

(h) Machinability.

As mentioned above points (d) and (e) were regarded as of marginal worth especially considering that they are exceedingly difficult to monitor.

As mentioned in Section 2.4, equipment has been developed (such as AlScan by Alcan) to allow rapid assessment of melt hydrogen levels. This type of equipment would have been very useful in the current research, however no such equipment was available. A Hot Vacuum Extraction rig was available, however this equipment had not been in recent use and this means of hydrogen evaluation was considered too slow to be employed for analysis of the expected number of samples. A result of this was that no suitable, direct, melt-hydrogen measuring means was readily at hand. Compromise in the form of inclusion/hydrogen assessment via RPT type testing was conceivable as simple Straube-Pfeiffer test equipment was available. Testing with this equipment (as described below in Section 4.2) revealed that, due to time considerations, only one third of the projected samples could conceivably be assessed by this process.

The most common means of quantifying melt fluidity is to cast a spiral, either in sand or a permanent mould. The length of the solid spiral is then a measure of mould filling and fluidity. This method is so sensitive to casting variables such as the exact melt-pouring temperature that precision of ±10% is all that can be expected. Given the inevitable inaccuracies associated with spiral casting and a lack of alternative means to readily quantify melt fluidity, this property was not included in the investigation.

Machinability is also difficult to assess as no definitive measures of this property have been established. Machinability is typically assessed in a qualitative manner, something which could have been conducted during this research, however the results would have been purely subjective and open to question. Since all of the cast specimens would require machining to produce the required tensile test pieces, any large variations in machinability could be noted. However, only marginal significance could be associated with such results as not all samples could be processed in a single batch.

The properties finally considered for assessment are listed below, with those anticipated to be of marginal value signified by an asterisk:

- Tensile strength
- Proof strength
- Ductility
- Hardness
- Grain size
- Modification level
- Porosity
- Machinability*
- Propensity to form porosity under vacuum*

Other factors which may have varied significantly within the composition range investigated but which were not considered of great significance given the bounds of this research include: corrosion characteristics, electrical resistivity and thermal cooling characteristics.

3.2 EXPERIMENTAL DESIGN

3.2.1 Initial Target-Composition Design

The ideal of this research would be to conduct experimentation so as to accurately quantify the effects of, and interrelationships between, all of the selected elements on the various mechanical and structural properties listed above. This ideal was not a practical proposition due to both a lack of relevant, previous data on which a simplified and optimised experimental design could be based, and limitations on the time and finances available. It was soon realised that, due to the inherent variability associated with commercial casting, particularly sand casting, even if the data existed upon which an optimised design could be based, results would have to be analysed from a statistical perspective and so be derived from a necessarily large number of samples. Factors which compounded the difficulties associated with establishing a concise experimental plan were the anticipation that the accuracy with which the dependent properties could be assessed

would vary greatly, as would the elements expected to be influential from property to property. For example, if modification alone were to be the topic of investigation, it was considered unlikely that more than a few specimens would be required to establish that iron and manganese do not play a major role in influencing the refinement of eutectic silicon. On the other hand, controversy surrounds the worth and magnitude of the effects of iron and manganese on strength and ductility, hence significant numbers of samples may be required to resolve this point in a definitive manner.

Initially the primary aim of this research was to establish and quantify the effects of phosphorus, thus incorporating significant investigation into the closely interrelated modifying elements sodium and strontium. The secondary aim was to resolve the effect of iron, and the iron-manganese interrelationship.

The first question which arose when planning the experimental procedure was how many samples would be required to produce results which would allow statistically significant analysis of the physical properties being investigated. Without prior knowledge of exactly what level of variability could be expected for each physical property relative to the effects of the significant composition parameters this question could not be answered. By virtue of the large number of compositional and physical properties being investigated, establishing the data required to design a truly optimised experimental plan would have involved almost as much work as conducting the proposed research itself! With this in mind, it was realised that the research had to proceed with a slightly revised aim, namely to extract as much quantitative information as possible, regarding each of the physical properties to be monitored, from the limited number of samples which could be produced. As this aim suggests, no assurance could be given that any practically feasible design would produce statistically definitive results for all of the physical parameters in question.

As multi-linear-regression (MLR) (see Section 7.1) was the anticipated method of results analysis it was realised that an experimental design based on full factorial principles was neither necessary or desired. If exact experimental solutions are available which stem from observations of unique combinations of the complete predictor variable set and only first order predictors are employed (i.e. no interaction terms) MLR can calculate the predictor

effects with as few observations as there are predictor variables. Similarly, if more observations are available, successively more higher-order predictor terms (predictor interactions) may be calculated. Exactly which interactions are revealed is dependent on the constitution of the observations in question. For example Montgomery[148A] suggests *"A complete replicate of a design with six parameters at two levels (a 2^6 design) requires 64 runs. In this design only 6 of the 63 degrees of freedom correspond to main effects and only 15 degrees of freedom correspond to two factor interactions. The remaining 42 degrees of freedom are associated with three-factor and higher interactions. If the experimenter can reasonably assume that certain high-order interactions are negligible, then information on the main effects and low order interactions may be obtained by running only a fraction of the complete factorial experiment."*. Such reduced experiments are termed fractional factorial designs.

The fractional factorial designs used in this research were purposely not optimised in order to deliberately produce excessive composition variations. This was done as an alternative to attempting target composition-optimisation and then producing replicates of each composition set. The reasoning behind this was that it would maximise the chances of detecting interrelationships which might otherwise go unnoticed. This was only possible due to the use of MLR analysis. By concentrating on the elements Si, Na, Sr, P, Mg, Mn and Fe some logical experimental design simplifications were possible. The first step was to decide in exactly what ranges the respective elements required investigation. This was largely dictated by the range limits imposed by BS-1490-LM6 and the knowledge that phosphorus levels in the commercial base alloys are unlikely to fall outside the range 4-15ppm. As the influence of modification dominates variations in the majority of physical properties, the elements known to be closely related to this phenomena (Sr, Na, P) were singled out for investigation at several levels. If a full factorial design were to be constructed with just five levels of each of these modifier elements, 125 samples would be required without production of a single replicate. This number could be more than halved by nesting the sodium and strontium sets. In doing this, the interaction of these two elements was eliminated from the research. As data exists on the topic of modifier interactions[18C] this compromise was considered worthwhile. Further simplification was possible, as it was expected that within the phosphorus range of interest, chemical analysis

(wet analysis by NZAS) would not be able to differentiate between more than three, distinct phosphorus levels.

Of the remaining elements for investigation it was hoped that the effects of both silicon and manganese could be adequately investigated using a minimum of three separate aim composition levels. Three levels were considered necessary with silicon, since varying levels of this element cause significant structural changes; namely a transition from hypo- to distinctly hyper-eutectic structures. It is reported that iron compensation by full 1:1 manganese addition is not required[46] hence it was expected that the influence of manganese would also be highly non-linear and thus require investigation at one intermediate level at least. Since iron is not usually encountered in a primary form until iron levels exceed ≈0.7% all of the anticipated structures in this research were expected to contain iron within the eutectic region, at least in the absence of manganese. As a result of this it was considered reasonable to assume that the effects of iron would be reasonably consistent (linear) within the range of investigation (0.1-0.6%) and so not require extensive examination at intermediate levels. Similar assumptions were made for magnesium with little weight being placed on production of samples with magnesium contents intermediate between zero and the 0.1% limit.

Using the above guidelines an experimental layout was constructed which essentially consisted of three fractional factorial designs with variables as follows:

Group 1

Element	*Aim Composition Levels*			*No. Variables*
Sr	0.025%	or Na	0.015%	(2)
Si	10.0%		13.0%	(2)
P	minimum	6.0 ppm	11 ppm	(3)
Mg	0%		0.1%	(2)
Fe	minimum		0.6%	(2)
Mn	minimum	0.2%	0.5%	(3)
			Total No. Samples in Group	*144*

As shown in the previous table the composition variables in Group 1 give 144 composition permutations. This group of samples set out to provide the main array of sample compositions. The major concessions made within this sample set were that modifier levels were fixed and only the limiting silicon levels were investigated.

Group 2

Element	*Aim Composition Levels*			*No. Variables*
Sr	0.025%	or Na	0.015%	(2)
Si		11.5%		(1)
P	minimum	6 ppm	11 ppm	(3)
Mg	0%		0.1%	(2)
Fe	minimum		0.6%	(2)
Mn		0.2%		(1)
			Total No. Samples in Group	*24*

Group 2 aimed to provide an abbreviated mid-silicon data set and to closely resemble compositions typically encountered commercially. Some of the results of this group were to be used in combination with those below for investigation into the effects of variation in modifier content.

Group 3

Rather than being a true fractional factorial set of compositions this group is made up of three very similar sets of experiments which contain 11.5% Si as did Group 2. None of the samples in this set contain the same composition as the Group 2 samples, something which would have been unavoidable in a factorially designed group. The main aim of this final group of samples was to provide sets of data on modifier and phosphorus effects and interactions. So that a direct measure of the effect of phosphorus in virgin unmodified structures could be obtained an extra sample which contained 11.5% Si and 11ppm phosphorus and no other additives was included in the final set within this group.

	Element	*Aim Composition Levels*	
(i)	Sr	0.005% 0.01% 0.02% 0.025% 0.03% 0.04% 0.05%	(7+
	or Na	0% 0.005% 0.01% 0.015% 0.02% 0.03% 0.04% 0.05%	8)
	Si	11.5%	(1)
	P	minimum	(1)
	Mg	0%	(1)
	Fe	minimum	(1)
	Mn	minimum	(1)
		Set Total	15
(ii)	Sr	0.005% 0.01% 0.02% 0.025% 0.03% 0.04% 0.05%	(7+
	or Na	0% 0.005% 0.01% 0.015% 0.02% 0.03% 0.04% 0.05%	8)
	Si	11.5%	(1)
	P	11 ppm	(1)
	Mg	0.1%	(1)
	Fe	0.6%	(1)
	Mn	0.5%	(1)
		Set Total	15
(iii)	Sr	0.005% 0.05%	(2+
	or Na	0% 0.05% 0.04%	3)
	Si	11.5%	(1)
	P	6 ppm	(1)
	Mg	minimum	(1)
	Fe	minimum	(1)
	Mn	minimum	(1)
		Set Total	5+1
		Total No. Samples in Group	*36*

Full Design Total Samples 204

The design of an experiment of this type made up of several fractional factorial designs, each designed to satisfy separate but related objectives, is called "sequential" experimentation and is covered in some detail by Montgomery[148B], Mead[149], Diamond[150] and Mason et al[151].

It was realised that experimental inaccuracy associated with the addition of alloy and impurity elements would result in the production of samples displaying considerable compositional variation. Composition scatter was used as a deliberate but indirect form of mid-range sample production with "extra" specimens being produced when deviation from the planned composition was considerable. No guidelines were established as to what constituted an "acceptable" composition but production of "extras" was naturally associated with compositions prone to variability, a point which was highly desirable from a statistical perspective.

3.2.2 Phosphorus Analysis Limitations and Project Expansion

Phosphorus analysis was to be conducted by the laboratory staff at NZAS Ltd. The method considered most suitable was a wet chemical technique (see Section 3.3) which was both complicated and had never previously been performed at NZAS. Due to the time requirements involved in each phosphorus analysis it became apparent that only a limited number of samples could be analysed, 30-40 being the anticipated maximum. To enable prediction of the phosphorus level in all of the samples to be produced, analysis had to take place on a specific subset of compositions. Twenty two compositions were thus initially selected for analysis. The criterion used to choose this subset was that all of the composition variables be represented in a range as wide as that which was to occur in the full sample set. The selected sample compositions formed the basis for melts two through ten, as discussed in Section 5.1. Each melt contained the same aim phosphorus level and where possible, only one variable was changed between successive samples in a melt. It was hoped that analysis of the phosphorus results from the selected samples would enable prediction of the levels in subsequent samples by quantifying the influence of each composition variable and establishing the required addition rates of the phosphorus master-alloy in question. For example, if the base 10% Si alloy was found to contain 5ppm P, and additions of 0.1% Mg to add a further 2ppm P, 0.2% Mn to add 1ppm P, etc, then the phosphorus level of any given composition within the experimental bounds could be estimated.

During the period following production of the phosphorus analysis samples NZAS refined their analysis procedures, while physical property quantification methods were developed

(see Chapter 6) and production of samples not containing deliberate phosphorus addition commenced at Canterbury. It became clear that after considerable effort the chemists at NZAS were not making the anticipated progress. Analysing samples which varied so widely in composition (particularly silicon) was introducing complications which could not be easily resolved. The final results achieved by wet chemical means varied from 4 to 11ppm phosphorus, much as expected, but the associated error range was ±4ppm, making their worth exceedingly dubious. When the results were evaluated, no clear correlations with the melt additives, including the addition of the phosphorus master alloy itself, could be found. Other means of achieving more precise phosphorus analysis were investigated yet none proved viable (see Section 3.3). Accordingly, continuing with the main research aim as "the evaluation of the effects of phosphorus" was out of the question.

Following the loss of phosphorus as an experimental variable, an alternative was required which would be of metallurgical significance without posing excessive addition or analysis difficulties. The obvious substitute element which met these requirements was titanium. However, as mentioned in Section 2.3, this element is almost always used in conjunction with boron, especially when deployed as a grain refiner in foundry alloys. At this point it was decided to expand the project and investigate both titanium and boron subject to the availability of suitable products with which to make boron additions. Titanium additives were available immediately but obtaining a boron master alloy of the desired AlB_2 type posed potential problems. Given the possible delays associated with the supply of suitable boron additives, production of non-boron samples commenced. Should boron addition have proven impracticable due to unavailability of a suitable addition product, the remaining sample results could have stood alone as a mode by which the effects of the remaining investigation elements could be analysed.

Since the grain refining action of titanium has been shown to be non-linear and commercial addition rates are much lower than the limits imposed by BS-1490-LM6 it was decided that titanium would require investigation at a minimum of three levels. The similarity of the experimental design requirements between titanium and phosphorus enabled direct exchange of the two elements without redefining the design layout.

Samples which had previously been scheduled to contain 6 or 11ppm phosphorus were adjusted to contain 0.1% and 0.2% titanium respectively.

When a supposedly suitable boron additive was obtained production of boron containing samples became possible (See Section 5.2). Design of the boron-containing target compositions became rather complex as only an additional 70-80 target compositions were desired. The eventual design consisted of sequential fractional factorial layouts, some of which were reduced so as to eliminate composition permutations which occurred elsewhere. Overall, 80 additional compositions were added with boron levels ranging from 0.01% to 0.05% (0.05% being the limiting level in BS1490-LM6). The design compositions, separated into six interrelated sets, are listed below as Groups 4-9.

Group 4

Element	*Aim Composition Level Levels*	
Sr	0.025% or Na 0.015%	(2)
Si	10% 11.5% 13%	(3)
Fe, Mn, Mg	All minimum	(1)
Ti:B	0:0.05% 0.1:0.02% 0.2:0.05%	(3)
	Total No. Samples in Group	*18*

This set of compositions investigated the interrelationships between the grain refiners and the silicon level. It also provided a comparison between the two modification elements.

Group 5

Element	*Aim Composition Levels*	
Sr	0.01% 0.025% 0.04%	(3+
or Na	0% 0.007% 0.015% 0.04%	4)
Si	12.7%	(1)
Fe, Mn, Mg	All minimum	(1)
Ti:B	0.1:0.02% 0.2:0.05%	(3)
	Minus Repeats	21(-2)*
	Total No. Samples in Group	*19*

Since the effects of silicon variations were regarded as having been investigated in Group 4 group five and all subsequent groups were produced without additives which would change the base alloy silicon level. A result of this is that several samples (≈ 80) were eventually

produced with approximately 12.7% Si, which is very close to the *actual* eutectic level. Group 5 aimed to investigate the interactions between the modifiers and grain refiners as well as providing more samples by which to compare the two modifying elements.

Group 6

Element	*Aim Composition Levels*	
Sr	0.025%	(1)
Si	12.7%	(1)
Fe, Mn, Mg	Minimal plus one of ...	
	0.1%Mg, 0.2%Mn, 0.5%Mn, 0.6%Fe	(4)
Ti:B	0%:0.05%, 0.1%:0.02%, 0.2%:0.05%	(3)
	Plus other combinations	(3)
	Total No. Samples in Group	*15*

As the modifiers were investigated above, Group 6 and subsequent samples were all designed incorporating a fixed strontium level considered typical of that which would be encountered commercially. Group 6 investigated the effects of Fe, Mn and Mg on the performance of the grain refining elements. While no combinations of Fe, Mn and Mg are listed in the above plan, several were included for which no simple structure could be devised (see the individual listings in Appendix B and Group 9).

Group 7

Element	*Aim Composition Levels*	
Sr	0.025%	(1)
Si	12.7%	(1)
Fe, Mn, Mg	With and without max. of all.	(2)
Ti	With and without max.	(2)
B	0.005%, 0.02%, 0.035%, 0.05%	(4)
	Total No. Samples in Group	*16*

This group investigated variations in the boron level and the effects of maximum and minimum levels of the other impurity and alloy elements.

Group 8

Element	*Aim Composition Levels*	
Sr	0.025%	(1)
Si	12.7%	(1)
Fe, Mn, Mg	Minimal	(1)
Ti:B	0.01%:0.01%, 0.02%:0.02%, 0.01%:0.05%, 0.03%:0.05%, 0.05%:0.05%, 0.1%:0.05%	(6)
	Total No. Samples in Group	*6*

Group 8 investigated the effects of varying both Ti:B levels and ratios.

Group 9

This final group contained various Fe, Mn, Mg combinations with 0.1%Ti and 0.02%B (see Appendix B).

Total Group Samples *6*

Total Boron Containing Samples ***80***

Several of the above composition sets contained titanium/boron combinations of 0%:0.05%, 0.1%:0.02% and 0.2%:0.05%. These three levels were selected deliberately because: the first represents the maximum permissible level of boron and must be achieved by alloying with boron alone; the second provides mid-range titanium and boron levels and corresponds to the use of commercial 5%Ti-1%B master alloy; and finally, the last pairing combines maximum titanium and boron levels and requires the use of both the boron and titanium/boron master alloys.

A full list of the final 284 aim-compositions separated into the various groups as described above is given in Appendix B.

Summary

In summary, the final research was based on an experimental design constructed from sequential fractional factorial designs, some being complete, others being simplified and reduced by nesting and selective omission. The overall design exploited the ability of MLR analysis to remove the need for replicating samples by instead producing a necessarily large number of samples, all of varying composition. A result of this was that

the samples produced spanned virtually the entire spectrum of LM6 alloys which may be encountered commercially. Concentrated sampling was directed at processes of particular interest such as grain refinement, iron contamination and modification. The only conceivable commercial alloys complying with BS1490-LM6 which have not been considered are secondary alloys containing appreciable zinc, copper or lead. The issue of phosphorus contamination also remains unresolved.

3.3 PHOSPHORUS ANALYSIS

As mentioned in the previous section, phosphorus analysis proved a difficulty for which no acceptable solution was found. The phosphorus analysis required by this research ranged from 4 to 20 ppm with an accuracy of at least ±2 ppm. Theoretically, several spectrographic and colorimetric analysis processes are capable of achieving the desired degree of accuracy. The colorimetric methods are both more complex and potentially more accurate. All composition analysis was performed utilising the equipment and expertise established at NZAS Ltd. The spectrographic equipment available within this organisation was unable to monitor phosphorus in "non-pure" alloys with the degree of accuracy required, hence it was necessary to utilise colorimetric methods. As mentioned earlier the time and resources required to perform colorimetric analysis dictated that only a fraction of the final cast specimens could be analysed and this resulted in the selection of a specific set of analysis compositions.

Colorimetric analysis techniques (often referred to as "wet analysis") involve:

(a) Dissolving the cast sample in a mix of hydrochloric and nitric acids, then ...

(b) Adding molybdenum blue to precipitate ammonium phosphomolybdate.

(c) The phosphate precipitate is then extracted by filtration and redissolved in dilute sodium hydroxide solution.

(d) Following resolution of the phosphorus the solution may be neutralised and analysed by any one of a number of methods.

A version of the complete procedure is outlined in the 1941 publication, "Analysis of Aluminium and its Alloys" by The British Aluminium Company[152]. The stated accuracy

of the procedure is given as ±1 ppm, however no indication is given as to the alloy ranges this accuracy relates to. Once the phosphorus is in solution, several standard analysis techniques have been devised, many of which are described within the American Public Health Association (APHA) publication "Standard Methods for the Examination of Water and Wastewater"[153]. The accuracy of these techniques is largely determined by the initial solution phosphorus levels - something which could be varied in this research by changing the prior digestion techniques.

While some of the procedures described in the APHA text are seemingly conducted as a routine part of water pollution analysis in the US, they are seldom encountered in New Zealand. Accordingly, it was not surprising that very little experience existed on these processes, either at NZAS Ltd or the University of Canterbury. Despite extensive efforts by NZAS staff to refine the colorimetric procedure, problems were experienced which resulted in an inability to achieve the required degree of accuracy. Consultation with Elwin L Rooy(ASM)* and Pierre Lassara (Aluminium Pechiney)* both of whom are familiar with the phosphorus analysis of aluminium, revealed that, subject to experience and extremely rigorous processing, accuracies of ±1.5 ppm should have been possible. An example of the care required is that solution specimens should not be machined, rather they should be sheared or cut in some way. Neither correspondent indicated the sensitivity of colorimetric analysis results to variations in Si, Fe, Mn, Mg, etc, yet it is conceivable that variation of these elements within the bounds of BS1490-LM6 could seriously compromise experimental accuracies and thus the degree of accuracy NZAS could achieve.

The final results achieved by NZAS are presented below, as are the anticipated phosphorus levels and the various additions made to each sample. The predicted phosphorus levels were determined by assuming melts initially contained 2ppm phosphorus and that no variation in this level occurred due to melt additions with the obvious exception of the phosphorus master alloy itself. It was also assumed that the phos-copper master alloy used for phosphorus addition would give recoveries of 20% (see Section 5.2).

* Personal Correspondence via fax.

Table 4.0: Returned Phosphorus Analysis Results

Samples	Result (ppm)	Aim (ppm)	Additions	
37-1-2	8	min	10% Si	+ Sr
43-2-2	7	min	↓	+ Mg
44-3-2	10	min		+ Fe
48-4-2	10	min		+ Mn
61-1-3	6	11.0		+ Sr + P
67-2-3	8	11.0		+ Mg
68-3-3	10	11.0		+ Fe
72-4-3	10	11.0		+ Mn
1-1-4	6	min		+ Na
7-2-4	-	min		+ Mg + Na
8-3-4	-	min		+ Fe + Na
12-4-4	11	min		+ Mn + Ba
109-1-5	4	min	13% Si	+ Sr
120-2-5	4	min	↓	+ Mg + Mn + Fe
97-1-6	9	11.0		+ Sr
108-2-6	6	11.0		+ Mg + Fe + Mn
169-1-7	4	min		-
170-2-7	-	min		+ Na
171-3-7	-	min		+ Na
172-4-7	10	min		+ Na
188-1-8	6	11.0		+ Na + P + Mg + Mn + Fe
189-2-8	-	11.0		+ Na
190-3-8	-	11.0		+ Na
191-4-8	5	11.0		+ Na
180-1-9	8	min		+ Sr
181-2-9	-	min		+ Sr
182-3-9	-	min		+ Sr
183-4-9	8	min		+ Sr
204-1-10	5	min		+ Sr + Ti
205-2-10	6	min		+ Ti

Quoted Precision ±4 ppm

Cast #
Pour # see Section 5.1
Aim Composition #

Using the given error range it is possible that the sample with the highest recorded phosphorus level (11ppm) contains less phosphorus than the sample with the lowest recorded result (4ppm), hence the output from this analysis work is of no practical significance. Had the results displayed distinct trends relevant to the overall sample composition it could have been hypothesised that the given error range was conservative; unfortunately no such trends could be found.

Alternative Means of Analysis

Since colorimetric analysis failed to provide results of the desired accuracy, phosphorus variation was excluded from further experimentation. A result of this was that only limited efforts were made to find a spectrographic analysis method. Both Rooy and Lassara (see above) mentioned that a plausible method to achieve the desired accuracy was to use vacuum-stage light emission spectroscopy. While this was not a possibility at NZAS Ltd, enquires were made to various spectrograph manufacturers regarding the likelihood of success using this means of analysis on the range of alloys in question. This was done in the tentative hope of locating an organisation in possession of suitable equipment which may have been utilised at a later date or in subsequent research. Applied Research Laboratories (Australia) responded to the above enquires by supplying spectrometer specifications which suggest that at best, ±3 ppm could be expected. No mention was made regarding the influence of varying sample composition on the possible phosphorus detection accuracy, thus it appeared at this stage that Rooy and Lassara's comments may well have applied to "pure" alloys but not to the range of compositions being investigated. No further efforts were expended on resolving this issue.

4.0 DEGASSING TECHNIQUES

4.1 DEGASSING LANCE CONSTRUCTION

4.1.1 Evaluation of Potential Lance Materials

One of the initial aims of this research was to model the processing environment and procedures encountered in a typical small commercial foundry. Inert-gas degassing has found widespread acceptance industry wide; it has virtually become an industry standard. A consequence of this and the compatibility of the process with both sodium and strontium modification was that utilising this particular procedure during sample production was considered a necessity. The optimum method would have been via a submerged porous impeller. Due to the small melt sizes envisaged (1-5 kg), this would have required development of a suitably miniaturised impeller unit. It was hoped that impeller degassing could be avoided by sacrificing some efficiency and utilising a slightly oversized porous lance.

To aid production of an effective degassing lance a series of simple experiments were performed to evaluate the performance of various materials when subjected to molten aluminium. Any material used in contact with molten aluminium and to be used in the current research had to comply with the following criteria:

- To be available at reasonable cost within a short time frame.
- If unavailable in suitable lance form it had to be easily transformed to that state.
- Capable of withstanding thermal shock and operation up to 800°C.
- Not subject to degradation or be wetted by molten aluminium.
- Not be a source of melt contamination.

General foundry tools used in contact with molten aluminium are frequently made of low carbon steel. These steel tools are usually coated with a protective layer of alumina-based paste. In situations where tools are exposed to constantly moving molten metal (e.g. at the point of purge gas introduction), or where avoidance of melt contamination is vital, tools

are usually manufactured from ceramic or graphite. By virtue of these points the following materials were selected for evaluation as potential lance materials.

- Low carbon steel,
- 304 stainless steel,
- Alumina-coated mild steel,
- Alumina-coated stainless steel,
- SL60ZA 60% alumina ceramic (mullite type),
- Graphite ... and later,
- Alumina-coated graphite.

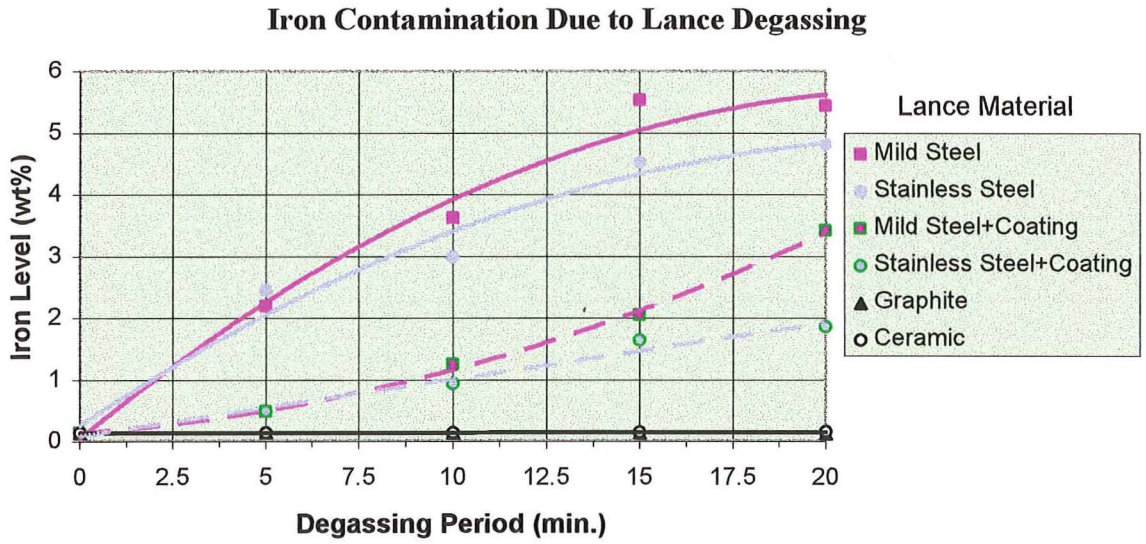
The alumina coating consisted of proprietary phosphate-bonded alumina-chromic oxide paste designed specifically as a foundry tool protectant (Abel-Lemon & Co "Alcoat-D").

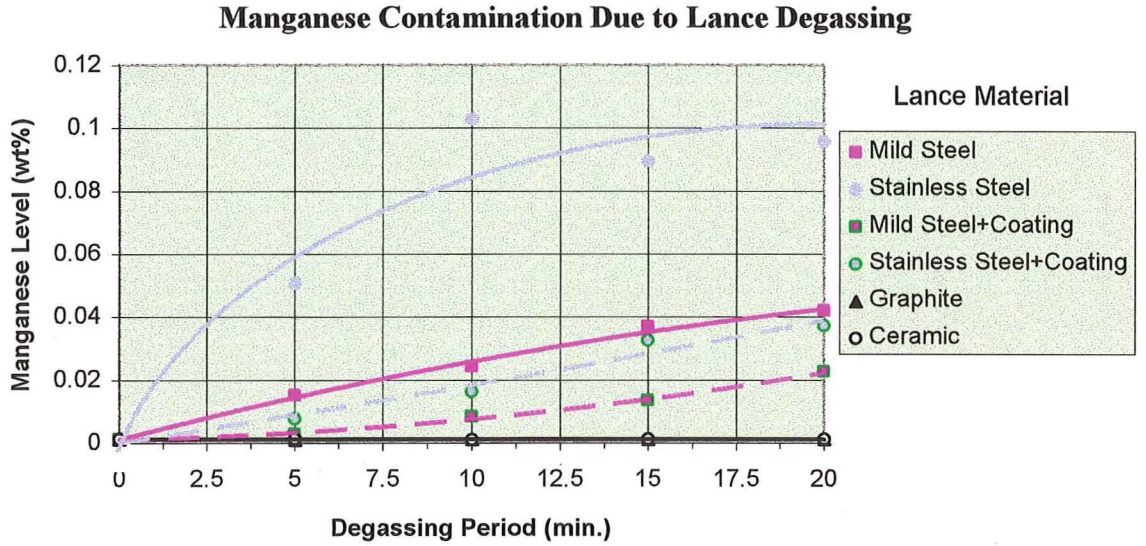
Experimental Procedure

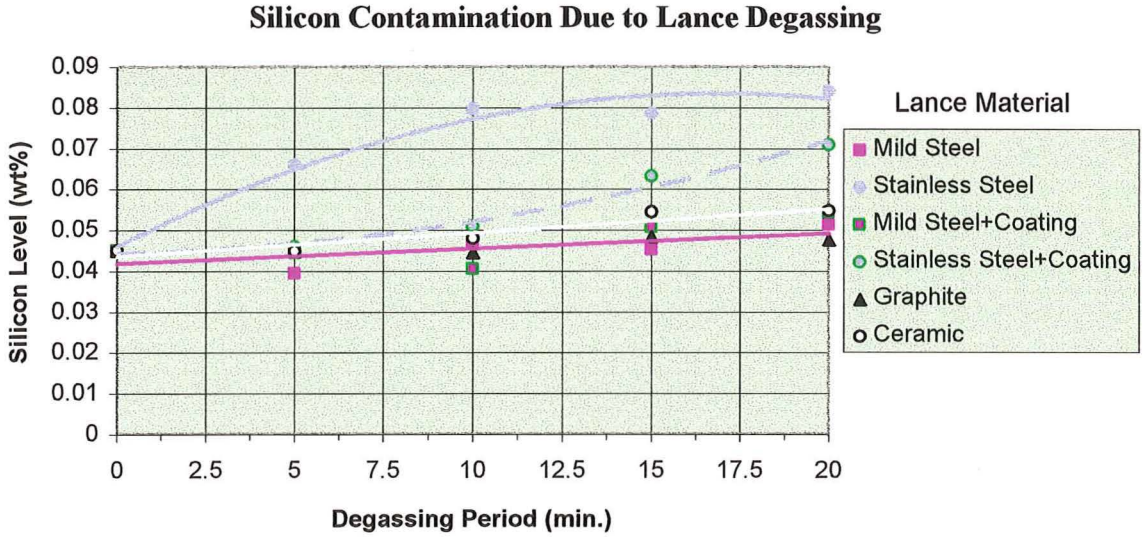
A conventional, small clay-graphite crucible coated with protective paste was used to melt 400g of commercially pure aluminium. The melt was then heated to 780°C and allowed to stand at this temperature for some five minutes. At this time a degassing lance constructed from one of the materials under investigation was submerged in the melt and an injection of 99.99% pure argon purge gas commenced. The lances were all similar, being open ended tubes of approximately 13mm outside diameter. The wall thickness varied as follows:

- Stainless steel 1 mm
- Low carbon steel 2.2 mm
- Ceramic 2 mm
- Graphite 3.8 mm.

Degassing was performed for a period of five minutes, after which any slag was removed and a 58g sample disc was cast using a small resin bonded sand mould. The remaining molten metal was then covered in a capping flux (Foseco Coverall 11) and allowed to solidify. The metal was then reheated and the process repeated; four cycles were carried out with each lance.







Figures 25,26 and 27: Overstated melt contamination by various argon lance materials.

One problem which arose during the testing was that each ceramic lance fractured during its second plunge. It was hoped that this problem could be avoided with larger melts by performing more thorough pre-heating and so reducing the degree of thermal shock.

Results

The composition of each of the small sand cast specimens was ascertained by New Zealand Aluminium Smelters Ltd using optical emission spectroscopy (O.E.S.). The results of these analyses are listed in Appendix D and the more significant composition variations are illustrated graphically in Figures 25, 26 and 27.

By using small volumes of aluminium and oversize lances these experiments were designed to overstate and emphasise the contamination due to the differing lance materials. Consequently, the results obtained do not reflect the level of contamination which could be expected in a commercial situation. The removal of such large samples (58g) in comparison to the melt size (400g) significantly reduced both the melt size and the area of lance exposed to the melt. Due to the tapering nature of the crucible the overall ratio of exposed lance area to metal volume increased as each successive sample was removed. This effect is compounded by the exposed lance surface areas becoming larger due to degradation having a roughening effect. These points should have led to an increased rate of contamination as testing proceeded. However, only the coated stainless steel results displayed this effect. It can be concluded that within the contamination ranges obtained (0-6% Fe, 0-0.12% Mn, 0-0.1% Si) the increased lance area per unit molten metal was more than offset by the effects of increasing contaminant levels slowing the rate of lance degradation.

What is obvious from the results is that the metal lances caused substantial iron, manganese and silicon contamination. As a result of this, even in an alumina-coated state, these lances were deemed unsuitable for further investigation. The only acceptable lances from a contamination viewpoint appeared to be those constructed from the ceramic and graphite. As can be seen, neither of these lances resulted in an appreciable increase in the levels of the monitored elements.

Physically, all metal lances displayed severe degradation (see Plate 5). Degradation of the alumina-coated lances appeared to be concentrated on the tube leading edge however following the fourth plunge the entire exposed surface was showing signs of attack. The uncoated lances experienced degradation over the entire exposed surface, with metal losses being more pronounced in certain interconnected regions ... no effort was made to explain this phenomena. Each of the uncoated samples ruptured part way up the tube side, thus allowing the purge gas to escape near the melt surface; the effectiveness of post rupture degassing must have been minimal (see Plate 6). Once the lances had ruptured, the rate of metal degradation below the rupture point slowed dramatically. This acted to stabilise the higher escape point and emphasised how influential melt turbulence was on the rate of lance breakdown. As can be seen in the results, the protective worth of the alumina coating faded with time but contamination was typically reduced by upwards of 60%. The benefit of applying this form of protection to steel foundry tools was clearly displayed although frequent recoating is obviously a necessity, especially when tools are employed in regions subject to high melt turbulence and/or prolonged exposure.

At this early stage of experimentation supplies of graphite were extremely limited and without incurring great cost, no replacement material could be sourced. Given the short supply and the physically fragile nature of the graphite which was available, efforts were concentrated on production of an acceptable ceramic lance. SL60ZA ceramic lances were readily available as they could be produced from relatively inexpensive thermocouple sheaths. Koppers (Germany), the manufacturers of the thermocouple sheaths claimed SL60ZA to have "good" thermal shock resistance, hence hope was held for improved durability given sufficient care prior, and subsequent to, immersion in future melts.

4.1.2 Production of a Foundry Lance

SL60ZA Ceramic

Tests were carried out in an attempt to find a suitable method of employing the ceramic lances in melts of the required size (1-5kg). Due to the failures encountered with the open ended lances mentioned above, the blanked-off end of the sheaths was retained and four staggered 4mm diameter holes were drilled through the sheath tip. It was hoped that the revised lance layout would strengthen the lance tip and produce a slightly finer bubble size.

Plate 5: Various degassing lances following 20 minutes melt exposure.
a) Low carbon steel. b) 304 Stainless steel.
c) Alumina coated mild steel. d) Alumina coated stainless steel.
e) Graphite (Note the burnt mid section). f) SL60ZA Alumina ceramic.

Plate 6: Ruptured low carbon steel lance - this lance ruptured following six minutes exposure to the melt.

As a further aid in reducing the likelihood of fracture the lances were either preheated to 200°C in an electric furnace or thoroughly heated directly in the flame of the gas fired furnace being used. Lances used in final sample production melts were required to withstand deeper emersion but the melt temperature would be some 40°C below that encountered in the earlier testing. Due to the short lance length used (375mm for economic reasons) very high temperatures were expected to be encountered at the lance attachment point. Direct bonding between the lance and its metal supply tube via refractories was deemed unlikely to be successful due to the widely varying thermal expansion rates. To avoid this problem both taper and Jacobs style chucks were designed to hold the lance.

When preheated lances of the form mentioned above and attached as mentioned, were trialed on 4kg melts at 740°C, continued thermal shock failures and difficulties maintaining firm lance attachment were encountered. Once again the failures generally occurred on the second immersion. The only positive point was that the lost ceramic floated cleanly (unwet) on the molten metal surface allowing it to be easily extracted. The logical solution to these problems was to change to longer lances made of a more shock-resistant ceramic. Such a change would have necessitated substantial expenditure on an inherently fragile product which would almost certainly have been inadvertently broken in the foundry environment. Thankfully this line of experimentation did not require pursuing as, by this stage, a supply of suitable graphite tube had been established.

Graphite

A supply of coarse graphite was obtained from New Zealand Aluminium Smelters Ltd. This consisted of 32mm O.D., 12mm I.D. tube, a size which proved extremely appropriate. A lance was constructed from this material by blanking off one end of a 600 mm long tube with a graphite plug and then drilling a series of 2.5mm diameter holes through the lance tip. An external 1" BSPT thread was then cut on the open end of the plugged graphite, allowing direct attachment to standard one inch pipe fittings, as shown in Figure 28. A Viton O-ring was incorporated into the lance connection flange so as to minimise any gas leakage.

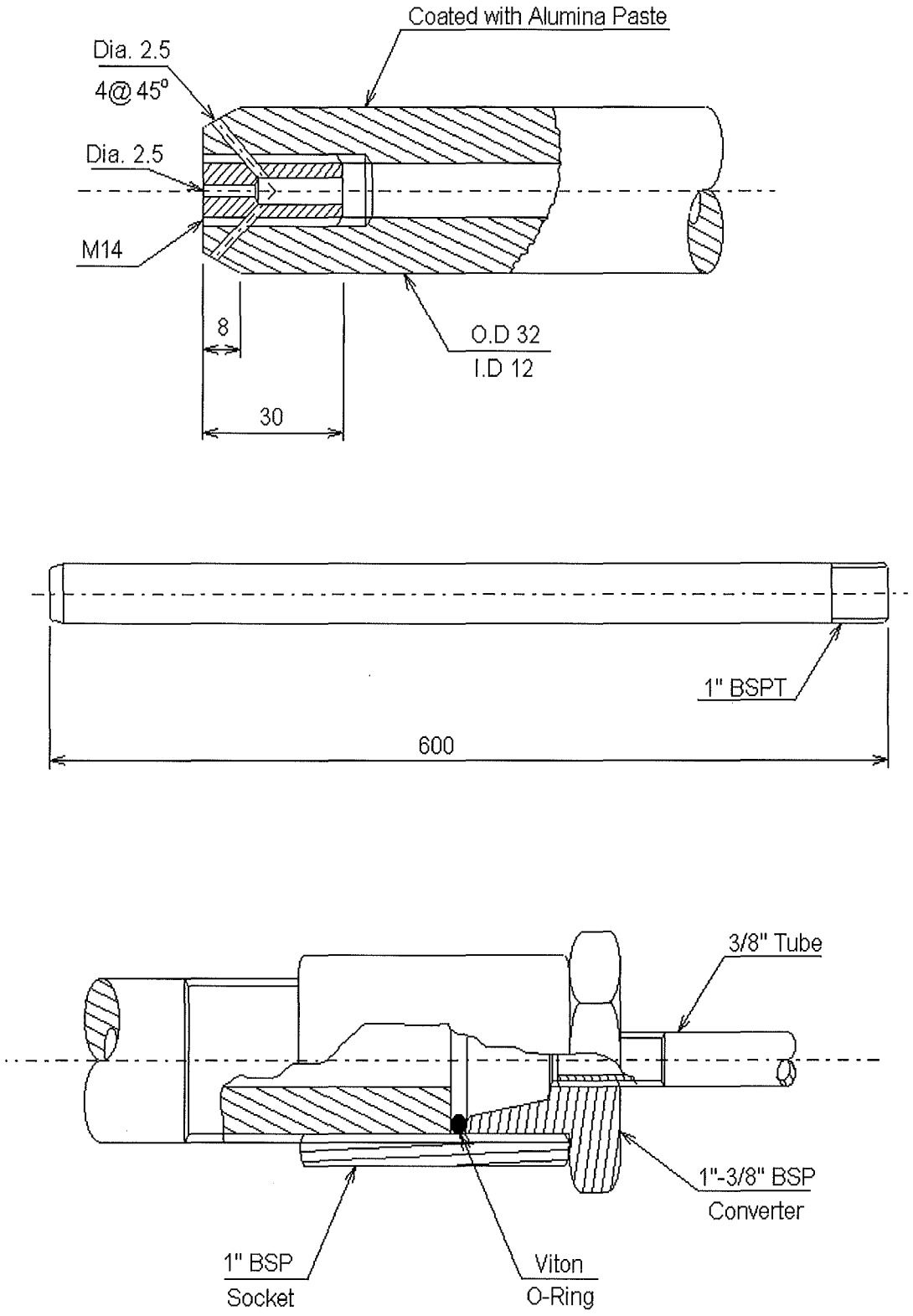


Figure 28: Final graphite foundry degassing lance format

Although it was unknown if the O-ring would endure the high temperatures transmitted along the lance, subsequent testing revealed no problems in this respect. It was observed during the testing outlined above that graphite tends to burn at the point at which it makes contact with the melt surface. In an attempt to prevent this occurring on the larger production lance, a coating of alumina paste was applied. The lance in this form appeared somewhat oversize, however since no melt contamination was envisaged this was not expected to pose a problem.

Testing with this lance proved totally successful with no lance degradation or melt contamination being detected. It was found that recoating with alumina paste was required every six degassings and that the majority of wear encountered was caused by abrasion during removal of excessive built-up alumina prior to recoating. Lances of this type were used throughout the entire sample production process, with lances enduring over 200 five-minute degassing cycles without the need to be preheated prior to immersion or be treated in an unduly gentle manner.

4.2 REDUCED PRESSURE TESTS FOR THE DETERMINATION OF DEGASSING TIMES

A series of experiments was performed with the aim of establishing the practical degassing ability of the graphite lance mentioned above. Due to the large size and simple construction of the lance, hydrogen removal efficiencies were not expected to be high. It was, however, hoped that hydrogen could be removed rapidly and effectively enough to simulate commercial inert-gas degassing. Initial tests set out to establish how much time would be available for degassing assuming it was performed from 760°C down to 720°C. Tests which comprised injecting 2.4 ℓ/min[†] of argon through Al-Si eutectic alloy over the temperature range of interest soon established that if the crucible was removed from the furnace during degassing, cooling was so rapid as to be a major problem. When the crucible was left within the gas-fired furnace substantially longer cooling periods were

[†] 2.4 ℓ/min was used as the argon flow rate as this allowed a steady flow of gas to be released into the melt which did not cause undue surface disturbance.

available. The exact time available was strongly dependent upon the amount of heat retained within the furnace, a variable which would be difficult to control during final specimen production. It was realised that during final sample production holding periods would often be required prior and subsequent to degassing so as to allow alloy and impurity additions to be made. When melts were conducted which simulated the alloy/impurity holding periods it was found that little more than five minutes would be available for degassing if excessively low modification and pouring temperatures were to be avoided.

To assess the hydrogen removal ability of argon injection via the graphite lance, RPT (Straube-Pfeiffer) samples were taken from a 4kg melt at various times from the start of degassing. Prior to degassing the melt had been held at 820°C for 4-5 minutes then allowed to cool slowly to 760°C whereupon lance degassing commenced. The RPT tests consisted of solidifying an ≈220g sample under a vacuum of 10-15 torr. Due to the time required to perform one of these tests only one sample could be taken from a single cooling cycle, hence the heating/degassing process was repeated six times with sampling times of 1, 2, 3, 4, 5 and 7 minutes from the start of degassing. Sections of the samples subject to more than 3 minutes degassing displayed minimal porosity while neither the 1 or 2 minute samples were sound.

From the above tests it was concluded that the simple graphite lance was effective at removing hydrogen and that with virgin, untreated Al-Si eutectic alloy only 3-4 minutes degassing with an argon flow rate of 2.4 ℓ/min was sufficient to produce sound castings. As porosity levels were to be monitored in all final cast samples it was hoped that adoption of a consistent degassing practice would allow porosity variations to be attributed directly to the various alloy/impurity additions made.

The initial samples produced displayed higher porosity levels than was expected and consequently, degassing times were subsequently increased from three minutes to what was considered the practical maximum of five minutes. This is mentioned in Section 5.1.

4.3 ALLOY COMPOSITION VARIATIONS DURING DEGASSING

It has long been known that degassing methods aid the removal of inclusions as well as some alloy elements; the modifiers being particularly sensitive in this regard. Very little data exists outlining exactly what composition variations can be expected during the degassing process so a set of experiments was carried out to compare the proposed argon lance degassing with various alternatives, such as lancing with nitrogen and the use of proprietary effervescent nitrogen and chlorine tablets. It was hoped that argon and nitrogen would display the same lance degassing characteristics because argon was the preferred experimental gas while commercial degassing is almost always performed using nitrogen due to cost reasons. Argon was preferred for the proposed experimental work for two reasons. Firstly, argon was available with very low and monitored moisture levels. Secondly, in the event of a gas cylinder requiring rapid replacement during sample production, several alternative argon supplies were readily available. The only disadvantage associated with the use of argon rather than nitrogen was the far higher expense; this was considered of little real significance given the relatively small total amounts of gas to be consumed.

Experiments to assess the impact of the various degassing methods on the base alloy composition involved melting a 4kg charge of virgin Al-Si eutectic alloy, then monitoring the metal composition prior to and during the degassing process. The virgin eutectic alloy was initially boosted to the maximum levels of magnesium, manganese, zinc and iron permitted by the BS-1490-LM6 standard. The grain-refiners titanium and boron, along with either sodium or strontium modifiers were also added in amounts typical of those found commercially. The methods by which the alloy additions were made were the same as those employed during sample production which is described in Section 5.2. The basic form in which the additions were made are listed below:

- Magnesium — Pure metal
- Manganese — Al-75%Mn compacted powder
- Zinc — Pure metal
- Iron — Al-50%Fe compacted powder

- Titanium and boron	Al-5%Ti-1%B master alloy rod
- Sodium	Pure metallic sodium
- Strontium	Al-10%Sr master alloy rod.

The degassing methods employed consisted of inert gas degassing with nitrogen and argon via the graphite lance detailed above or additions of proprietary nitrogen and chlorine releasing tablets (Foseco "Degasser 610 and 190" respectively). The nitrogen-releasing tables (610) are specifically designed to be used with strontium premodified ingot thus minimising modifier depletion and eliminating the need for expensive inert-gas hydrogen-purging equipment. All lance degassing was performed with the standard gas flow rate of 2.4 ℓ/min while composition samples were extracted, each 1.5 minutes of degassing time. The solid tablet degassers were added in doses of 1/3 the recommended total addition (12g) then composition discs were cast 1.5 minutes later. Due to the amount of time required for degassing and sampling to take place it was necessary to reheat the melts after either 6 or 7.5 minutes degassing (4 or 5 tablet additions). Reheating consisted of raising the melt temperature from ≈680°C to 800°C; this took approximately 10 minutes.

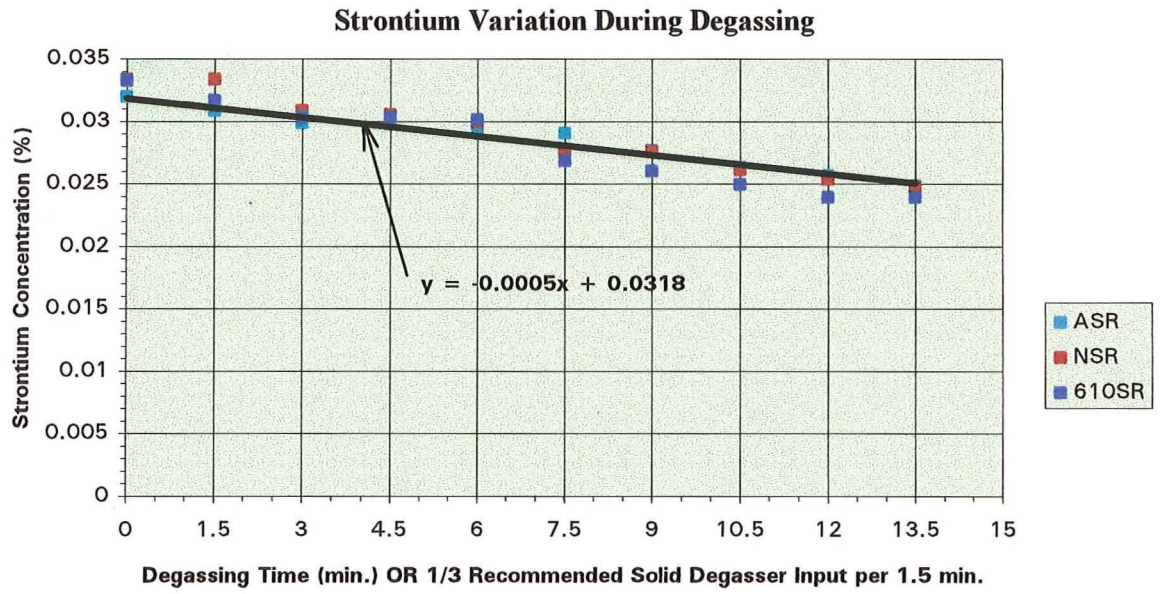
Conventionally, sodium modified melts are not degassed with nitrogen tablets and, similarly, strontium modified melts are not degassed by reactive gases such as chlorine (as released by the 190 tablets). A consequence of this was that the experimental permutations of Foseco 610 vs sodium modified melts and Foseco 190 vs strontium modified melts were not investigated. While sodium modification is conducted following degassing, sodium depletion was monitored during degassing as it is conceivable that melts may contain substantial in-house returns which have been subject to earlier sodium modification. In the secondary aluminium industry, excessive magnesium is removed by the addition of chlorine, hence it was expected that when chlorine degassing (190) was used the rate of magnesium depletion would be higher than for the alternate processes. In an attempt to highlight this effect and separate the magnesium results into two separate sets the aim magnesium level for the chlorine degassed samples was lowered to 0.05%. Unfortunately, the two samples with aim magnesium levels of 0.05% achieved actual levels of only 0.03%.

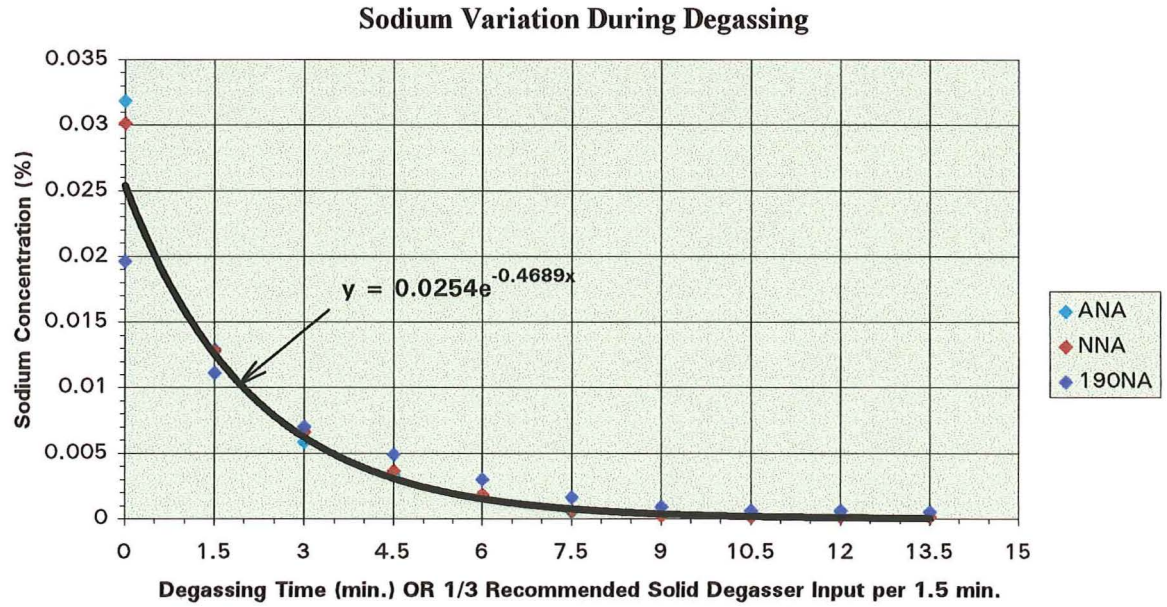
Cast Notation Used

A_ _ = Argon degassed.
N_ _ = Nitrogen degassed.
_NA = Sodium added as initial modifier.
_SR = Strontium used as initial modifier.
190_ _= Degassed with Foseco "Degasser 190" -This product uses chlorine as the purge gas and also acts as a grain refiner.
610_ _= Degassed with Foseco "Degasser 610" -This product uses nitrogen as the purge gas and is designed specifically for use with strontium premodified ingot.

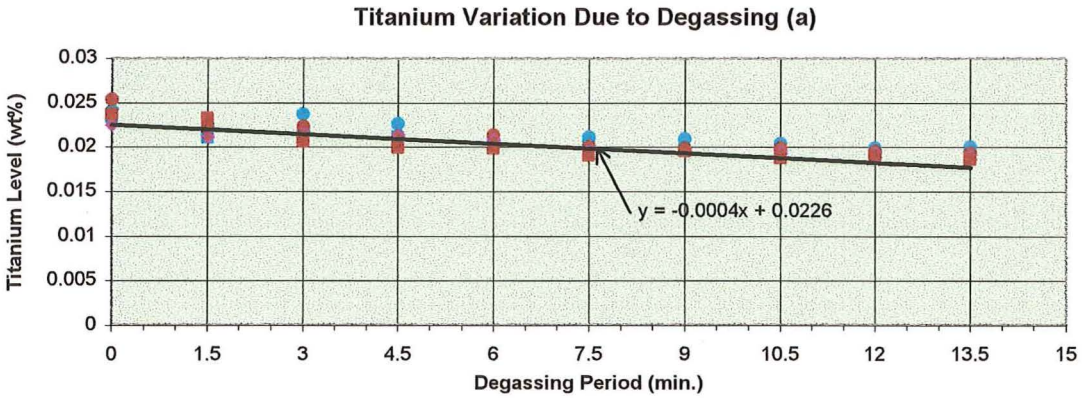
gas flow rate used =2.4l/min. (0.142m3/hr)

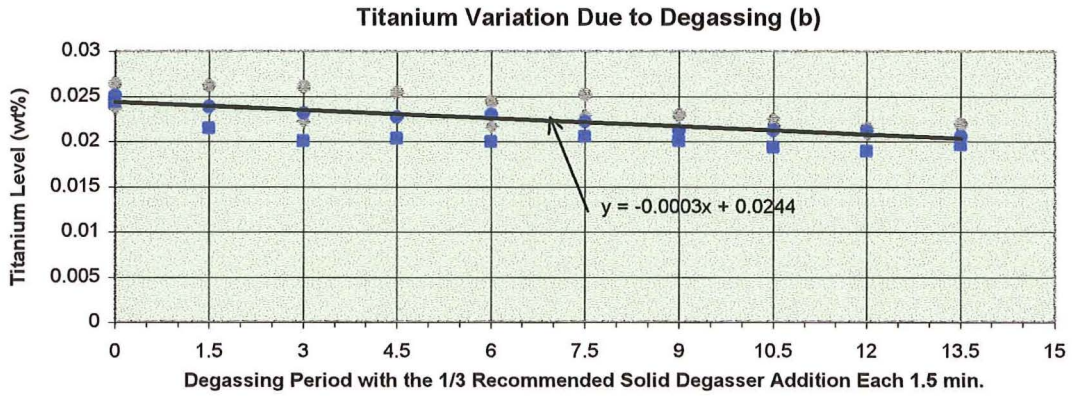
Note: A Ten Minute reheat of the below casts took place after six minutes degassing. time.

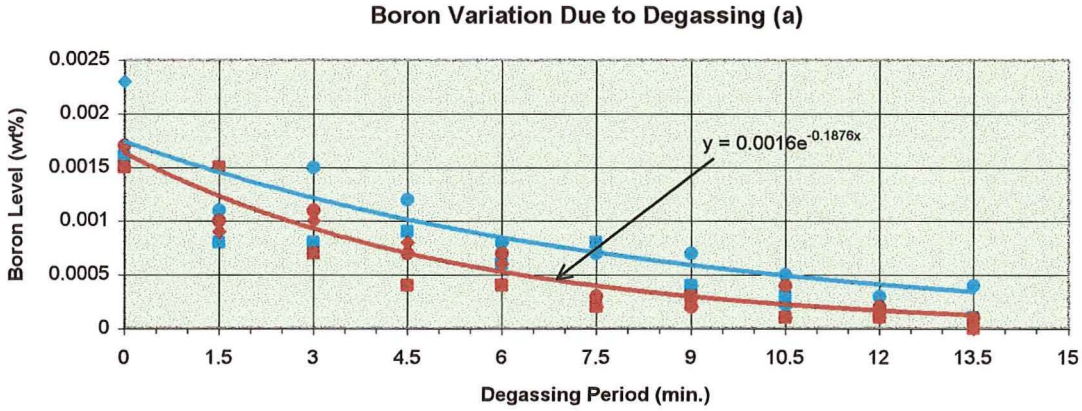


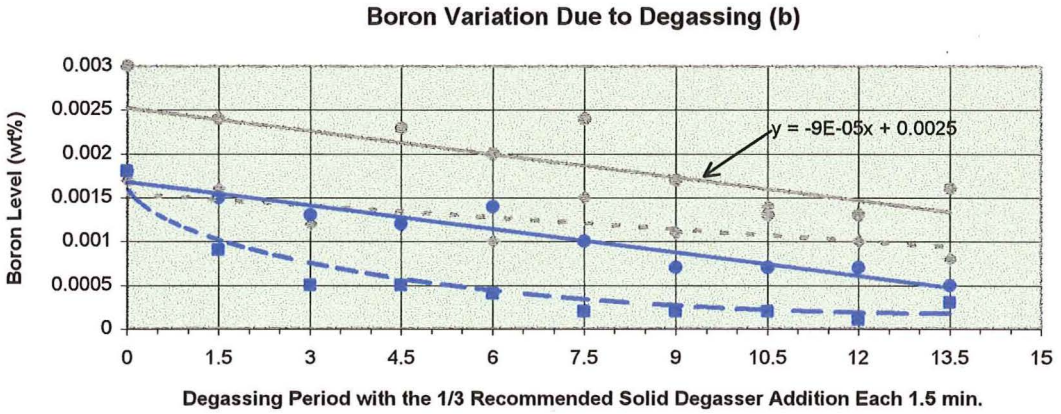


Figures 29&30: Modifier removal due to degassing.

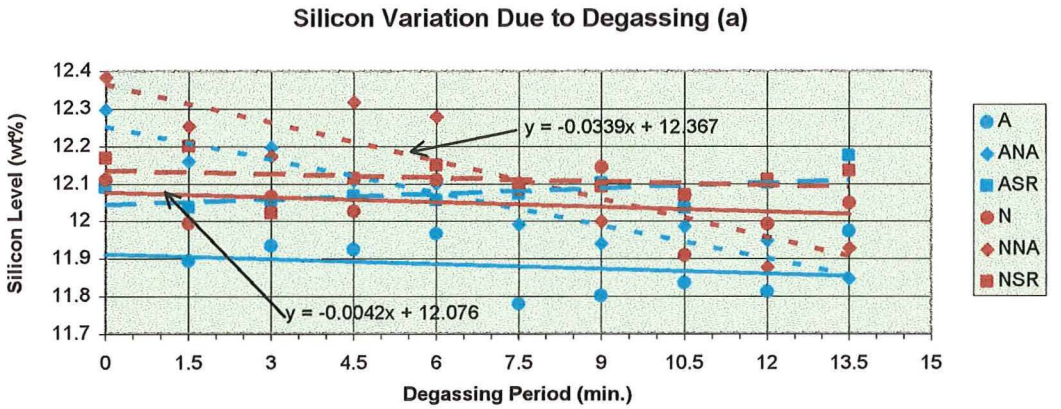


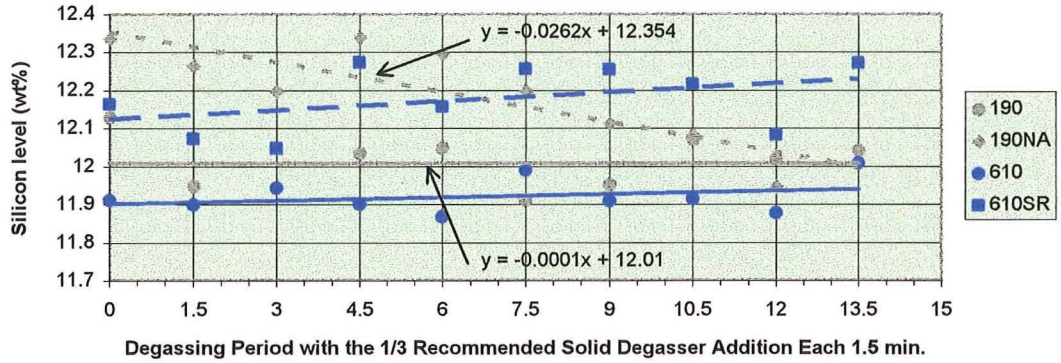


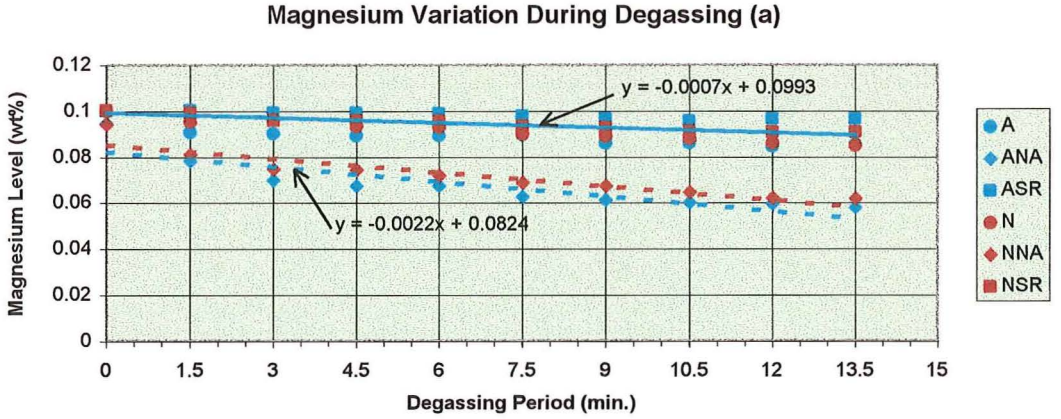


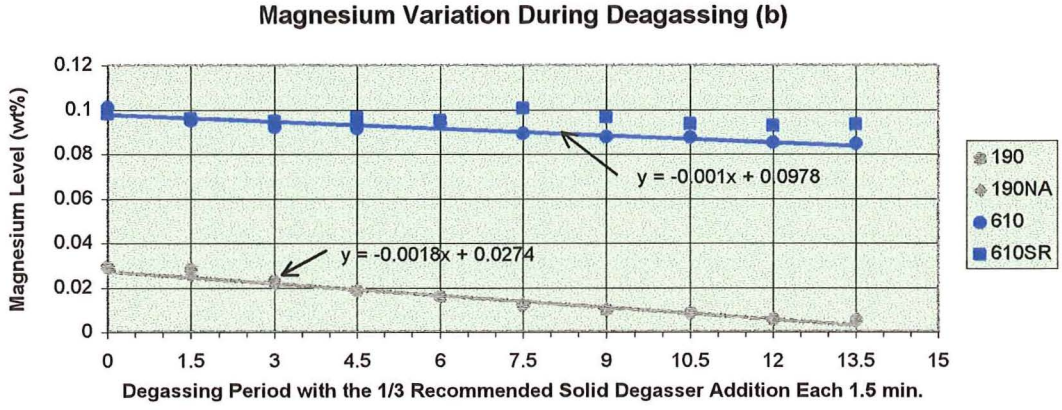


Figures 31a, 31b, 32a and 32b: Grain Refiner Removal Due to Degassing.









Figures 33a,33b,34a and34b: Alloy Removal Due to Degassing.

Results

The tabulated composition results from which Figures 29-34b have been generated are contained in Appendix F. These results stem from full 21 element OES analysis at NZAS Ltd.

The convention used when labelling the depletion curves is that the first letters or numbers indicate the degassing method (A, N, 190, 610) while remaining letters indicate the modifier present (NA or SR). Where it has been possible to fit clear trend lines to the plotted results, the equation of the trend line has been included. Only the elements which displayed significant change in concentration during degassing are displayed in Figures 29-34, notably zinc, manganese and iron all appeared unaffected.

The conclusions which can be drawn from these results are summarised below.

- The gradual decrease in strontium levels, as shown in Figure 29, was consistent at 0.0005% per minute irrespective of the inert gas type or the method of gas introduction. This adds credence to the assumption that the addition of 1/3 of the total recommended solid tablet is equivalent to 1.5 minutes of lance degassing. The low rate of modifier removal also supports the practicality of using strontium premodified ingot, provided situations where exceedingly long melt holding times with intermittent degassing are avoided.

- Sodium depletion, as shown in Figure 30, displayed exponential decay with slightly slower modifier loss being observed with the use of reactive gas tablets (190) as opposed to inert gas lancing. The slight variation between the inert and reactive degassing may not be readily explained as the rates of gas introduction between the two methods are not directly comparable. Magnesium and sodium are thought to interact (see below) hence it would have been interesting to compare sodium extraction rates with and without the presence of magnesium. The lower sodium removal rate encountered with the chlorine tablets may be a result of any one or a

combination of the following points: the magnesium level was approximately one third that of the inert-gas degassed samples (implying magnesium assists sodium extraction); experimental error associated with variability in the addition and dilution of metallic sodium or an inherent property of sodium removal by chlorine. The only way to resolve these issues would involve further experimentation, something which was unfortunately beyond the scope of this work.

What can be concluded is that argon lance degassing is tantamount to the use of nitrogen and, irrespective of the type of degassing employed, sodium removal is so pronounced it precludes the practice of modifier addition prior to degassing.

- The grain refiners titanium and boron both displayed considerable fade with time, as shown in Figures 31 and 32. This may have been caused by boride settling, however the stirring nature of the degassing process makes this unlikely. The most plausible explanation for the extraction of these elements is that they formed particulate which floated out in a similar manner to conventional inclusion removal. It is difficult to determine if boron is influential in the loss of titanium, however, since boron levels were typically very low at the end of testing, an indication may be forthcoming if degassing and sampling were continued for longer periods. Very minor additions of nucleant can achieve significant grain refinement, therefore the seemingly minor, linear nature of titanium removal may be significant to foundries using minimal titanium addition rates. Similar decreases in titanium and boron levels occur irrespective of the inert gas present or the method of gas introduction employed. The proprietary chlorine tablet results show evidence of promoting increased boron retention; this may be due to boron introduction or reduced initial boron extraction. The former of these possibilities seems more likely, especially given the fact that the manufacturers (Foseco) advocate "Degasser 190" as both a refiner and degasser. Interestingly, this product does not appear to influence the level of any other elements associated with grain refinement.

- As shown in Figures 33a and 33b degassing had a minimal effect on silicon levels except in the presence of sodium. When sodium was present, silicon levels dropped by approximately 300ppm per minute of degassing. Taken at face value, this effect may be real in the sense that sodium may influence silicon

concentrations, or alternatively, the presence of sodium and its related modification may influence OES analysis results. It is unlikely that silicon morphology (i.e. modification) affects the OES results as the strontium-modified samples do not display the same trends as those encountered in the presence of sodium. The possibility that sodium may influence OES silicon readings is supported by the fact that samples containing sodium displayed higher initial silicon levels, the likelihood of which is hard to accept.

- Chlorination of molten aluminium and the formation of $MgCl_2$ to remove excess magnesium is de rigueur in the secondary aluminium industry. Accordingly, magnesium levels were expected to drop significantly when the chlorine reactive degasser (190) was used. As mentioned in Section 2.5, the formation of NaCl is thermodynamically far more favourable than $MgCl_2$. This would indicate that when chlorine is introduced to a melt, sodium should be removed before magnesium. Figures 34a and 34b show that magnesium removal was indeed enhanced by the introduction of chlorine. However, contrary to the above comments, sodium addition did not sacrificially protect the magnesium, rather it acted to expedite magnesium removal! This was not entirely unexpected as it is recognised practice to avoid sodium-containing cover-fluxes on alloys containing magnesium if magnesium retention is of importance. The ability of chlorine to remove magnesium and sodium is a well reported fact[93, 125], however no clear reference regarding an interaction between the two process has been found. Clearly an interaction between sodium and magnesium exists which is not fully understood or appreciated.

The overall conclusion of this work regarding the differing degassing techniques, particularly the substitution of argon for nitrogen when using lance degassing, was that, irrespective of the method of introduction, the three inert gas methods were all equivalent and interchangeable, whereas the reactive gas tablets promoted significant compositional variations. Although no contamination was detected which could be assigned to the nitrogen releasing tablets, they were not considered for the degassing operation in the final sample production as their consistency in composition and application could not be assured.

5.0 SAMPLE TEST PIECE PRODUCTION

5.1 CASTING PROCEDURE

All casting was carried out in a small foundry equipped with a conventional LPG-fired crucible furnace. To reproduce a typical small commercial foundry environment as accurately as possible, all tools and equipment were of conventional layout and construction. The crucibles were of the clay/graphite type whilst, with the exception of the degassing lance, the tools were constructed of low carbon steel. All tool and crucible surfaces exposed to molten metal were precoated with an alumina-based refractory paste - Abel-Lemon "Alcoat D" (see Section 4.1). During the casting process the tools were cleaned and recoated on a daily basis, while the crucibles were similarly treated after a maximum of four melt cycles.

Each melt cycle commenced with preheating of the furnace, crucible and tools. In an effort to reduce fluctuations in melt cooling rates due to variations in heat built up within the furnace, daily preheating of the furnace for at least forty minutes was found to be necessary. Initial melt charges consisted of base alloys of the following types in the appropriate ratios so as to achieve the desired 10, 11.5, 12.7 and 13% silicon levels:

- NZAS CA401F (Al-12.7%Si)
- NZAS ZP190B (99.91%Al)
- KBM Al25Si (Al-25%Si nominal).

Charge sizes varied from 1.1kg if a single specimen was to be cast to 4kg when four specimens per melt were required. Once the charge had reached 760-770°C (780°C for the 1.1kg melts) it was skimmed to remove the surface dross and the calculated iron, manganese and grain refiner additions were made. The alloying additives were plunged below the melt surface whilst at the same time attempting to minimise surface disturbance. These additions were made prior to degassing in the knowledge that loss of these elements would be minimal (see Section 4.3) and the melt stirring caused by degassing would promote full solution of the additives in a homogeneous fashion. In one instance difficulties were encountered as the iron additive refused to go into solution; this proved

difficult to explain and only occurred on one occasion. As is normal practice, no melts were allowed to exceed 790-800°C.

Once alloyed, the melts were degassed for five minutes after which the temperature had typically fallen to 725-735°C; in the few instances where temperatures exceeded this range degassing was prolonged as required. Degassing was performed with the crucible still within the furnace using the degassing lance and argon flow rates (2.4ℓ/min) described in Chapter 4. The argon gas, supplied from cylinders was certified to contain no more than 3ppm oxygen and 3ppm moisture. In an attempt to minimise moisture release the argon cylinders were exchanged as soon as supply pressures began to fall at an appreciable rate.

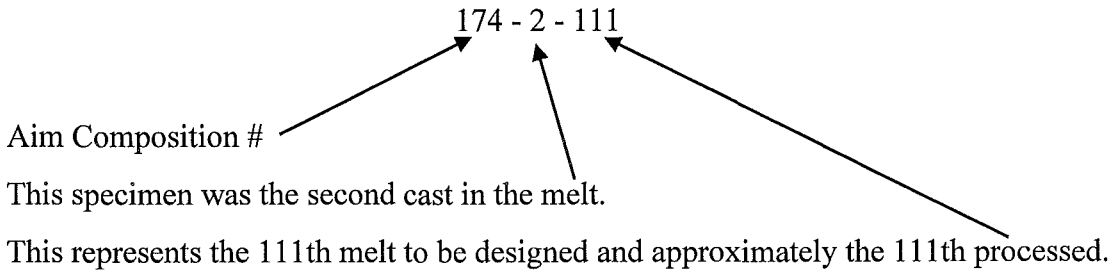
As soon as degassing was complete, the melt dross was removed and any required magnesium, phosphorus or modifier additions were made. As with the earlier additions, additives were immediately plunged below the melt surface with particular care being given to both sodium and magnesium additions. The melt was then left in a quiescent state for five minutes to allow modification and the dispersion of magnesium throughout the melt. Following the holding period, the melt was skimmed a final time; at this stage melt temperatures were in the range 710-725°C. The crucible was then removed from the furnace and the molten metal poured directly into sand tensile-test bar, permanent composition disc and metal Straube-Pfeiffer cup moulds.

If additional samples were to be produced from the melt the crucible and remaining molten metal were returned to the furnace and reheated to 760-770°C so that the above process could be repeated. Due to the drop in silicon levels during molten metal processing, silicon compensation was carried out by the addition of Al-25%Si master alloy between the processing cycles. Approximately twenty minutes was required between production of consecutive samples from a single melt. When the final cast in a melt had been carried out any excess metal was poured. This allowed the remaining surface residue within the crucible to rapidly cool and solidify so that it could be easily extracted. In an effort to minimise the possibility of contamination between consecutive melts, crucibles were only exposed to one type of modifier between thorough cleaning and refractory recoating. Since

production of samples which did not contain boron was completed prior to those which did, carry-over of this element should not have occurred.

A melt fluxing and capping product was applied to some early melts, the agent used being Foseco "Coverall 11". This product was applied while the melt was being heated and again during the quiescent period prior to casting. Use of this product was discontinued due to contamination of test bars by particles of cover and dross. This problem was brought about by a build-up of flux forming on the crucible wall which proved extremely difficult to extract, only to become dislodged during specimen pouring. It is unlikely that this problem would be encountered when melting larger volumes of metal as the crucible would be easier to clean and the amount of flux added per kilogram of metal would be substantially lower.

The identification system used when labelling the cast samples consisted of three successive numbers; the first giving the aim composition designation, as listed in Appendix B, the second and third giving the cast and melt numbers respectively. For example:



Several additional samples were produced by sampling collected scrap from the main casting process. These samples were labelled RM##. Two further samples were obtained from a local foundry which processes alloy of the same type (from the same source) in a similar way to that being investigated here. These samples were labelled HAM1 and AX65.

5.2 ALLOY AND IMPURITY ADDITIONS

When establishing the melt sequences, care was taken to create consistent patterns in the timing of alloy additions wherever possible. For example, the third sample in the majority of four-sample melts required additions to boost manganese levels by 0.3%. By maintaining consistent addition procedures and creating plots of the compositional changes versus addition amounts, optimum addition rates were quickly established as were any tendencies for certain additives to have inconsistent retention rates. No standards were established to outline what constituted acceptable composition results. The large number of "extra" samples created, was due partly to necessity and partly a desire to produce as many samples as practicable thus providing as much data as possible on which to base the MLR analysis.

The full specifications of the various base materials and addition products used during production of the cast specimens are contained in Appendix F.

The Base Products - Al and Si

As mentioned in the previous section, the base metal consisted of the appropriate proportions of commercial Al-12.7%Si foundry alloy, 99.91%Al foundry alloy and proprietary Al-25%Si master alloy. In an effort to reduce contamination in the base alloys, consideration was given to adding silicon directly to pure aluminium so producing high purity Al-Si eutectic to which all other additions could be made. This was not pursued as it was envisaged that alloying silicon would be time consuming (as discussed by van Lancker[154]) and would require extremely high purity silicon; something which was not readily available. Discussions with NZAS staff have subsequently indicated that they require only short dissolution times even when adding very coarse silicon to metal at temperatures below 1000°C, hence future researchers may find this option worth pursuing. A promising alternative which has come to light during the course of this research is to use a specially designed silicon addition product produced by the Nikkin Flux Corporation and marketed under the Niksil™ name. Indications[155] are that even when adding silicon at eutectic levels at temperatures under 800°C, the Nikkin product dissolves in less than five minutes. From an experimental perspective the major attraction of this product is that it is

available with exceedingly low levels of impurity, i.e. 0.01%Fe. A point worth noting on the issue of iron contamination is that NZAS CA401F (12.7%Si) as used in the current research, now appears to contain substantially lower iron levels than was the case at the outset of this research, i.e. 0.09% c.f. 0.18% (see sample AX65, Appendix H).

While van Lancker[154] indicates that long periods at up to 800°C may be required to fully break down the Al-25%Si structure, metallographic analysis carried out on some early samples to which Al-25%Si had been added showed no evidence of undissolved or excessively coarse silicon. This finding agrees with the data published by the master alloy manufacturers[156] which suggests that no more than ten minutes at 750°C is necessary for complete solution of additions at levels greater than those required during this research.

Iron and Manganese Addition

Iron and manganese were added as compacted powder briquettes: each of these products was easily added and displayed very consistent and high recovery rates. By virtue of this, few samples required reproduction due to iron or manganese inaccuracies. Addition of the briquettes took place prior to degassing in the hope that this would allow complete additive breakdown and homogeneity within the melt. Metallographic analysis of initial (and latterly all subsequent) samples prepared using the powder products revealed no evidence of inhomogeneity or inconsistency and hence these products continued to be used wherever necessary. The briquettes were obtained via NZAS Ltd, where they are routinely used for alloying primary aluminium.

Magnesium Addition

Magnesium additions were made in the form of pure magnesium (99.95%Mg) which was immediately plunged below the melt surface. In order to minimise the formation of oxides, (such as spinel) pieces of magnesium were added individually with care being taken not to allow magnesium fragments to sit on the melt surface. To minimise losses, addition took place following degassing and prior to modifier addition. Once initial addition rates had been determined, no problems were encountered and the recovery rates obtained were consistent at approximately 94%. Consequent additions could thus be made with some accuracy.

Sodium Addition

Sodium addition is recognised as being particularly problematic as recovery rates are notoriously inconsistent and yet optimum results require precise addition levels. Neither premodifying the alloy or creating master alloys are feasible addition methods hence sodium salts or pure metallic sodium must be employed. The former is often incorporated in flux injection processes but has lost favour in most other applications due to addition difficulties. Metallic sodium is commonly added in the form of small (15-50g) vacuum-packed aluminium canisters. The canisters prevent moisture pick-up by the hygroscopic sodium and thus reduce melt contamination. They also suppress reaction with the molten metal until the capsule is fully immersed, reducing sodium "flare-off" on the melt surface.

Due to the small scale of the melts and the varying sodium levels desired in this research, vacuum-packed canisters were not available in the small sizes required. Addition was carried out by extracting the appropriate weight of sodium from 25g vacuum canisters immediately prior to addition. Between casts, open canisters were stored under paraffin as the large numbers of melts excluded the possibility of opening fresh canisters for each melt. To reduce hydrogen contamination, all sodium surfaces exposed to the paraffin were either discarded or dried as best possible. The sodium was then tightly wrapped in several layers of aluminium foil. Foil wrapping the sodium had the added advantage of allowing the sodium to become fully immersed prior to the onset of the furious breakdown reaction in a similar way to that achieved using the commercial canisters.

With a few notable exceptions, all sodium additions took place following degassing and magnesium introduction. Early casting data indicated that, as expected, sodium recoveries were highly variable. In an attempt to overcome this problem a few melts were produced using excessive sodium addition immediately prior to degassing. The intention was to reduce the sodium content to the required level by degassing. However, these melts displayed no improvements in the consistency of recovery and were unable to achieve sodium contents at the levels required. Achieving the desired sodium levels with any accuracy proved to be a problem throughout sample production, particularly when levels in

excess of 0.03%Na were sought. Typical accuracies were no higher than ±0.004%, with substantially greater variations at high (≥0.03%Na) levels.

A problem which was encountered during the addition of sodium was a tendency for unreacted sodium to attach to the addition plunger so facilitating contamination of subsequent melts.

Strontium Addition

Whilst several master alloys exist for the addition of strontium, the composition most commonly used is Al-10%Sr, this alloy being available in either waffle, ingot or rod form. Al-10%Sr rod was selected for use in this research, partly due to availability and partly because it is reported to be effective within 1-2 minutes of addition[29]. As with the sodium addition, sections of the 10mm diameter rod were introduced following degassing and magnesium addition. Dissolution was rapid with no difficulties being encountered, irrespective of the desired level of addition. Strontium recovery rates were in the range 65-70% and were sufficiently consistent to allow much more accurate additions of this modifier than was possible with sodium.

Phosphorus Addition

Phosphorus additions were carried out at the same time as magnesium additions, i.e. immediately following degassing. The additive used consisted of foil-wrapped Cu-14%P prills. The master alloy prills were extracted from a Foseco Phoscopper alloying product known as "DS1". When calculating the amount of shot to be added the predicted recovery rate of 20% was used, this meaning that at most, one gram of additive was all that would be required. The 20% recovery rate was obtained from comments in a text by Gruzleski[18U] and information supplied by DP Parton at the London and Scandinavian Metallurgical Co Ltd Technical Centre. As no acceptable phosphorus analysis technique was established, no indication was gained as to the actual recovery rates achieved. The copper contents of the melts to which CuP had been added did not increase as was anticipated, which may be an indication that the prills did not go into solution. If this is the case, phosphorus increases will have been minimal.

Titanium and Boron Addition

Titanium and boron may be added in a myriad of forms, both individually and combined. The form of the addition has a strong influence on the response of the alloy, hence the most effective form of addition in one situation may prove inappropriate elsewhere. These issues were covered in Section 2.3. For this research the aim of titanium and boron additions was to promote grain refinement; consequently attempts were made to use products conducive to this outcome. In foundry applications, titanium is almost always added in conjunction with boron, often in the form of master alloys with nominal compositions of 5%Ti-1%B; accordingly this form of product was used in the current work when both titanium and boron were required in a melt.

Effective titanium addition can be achieved using either master alloys or compacted powders. During this research the product in use at NZAS Ltd consisted of Al-75%Ti compacted powder tablets. Due to the ready availability of this product it was tried for suitability in the experimental melts. Trial additions were made prior to degassing with the resulting structures displaying excellent refinement of a homogeneous nature. No difficulty was encountered adding this product, dissolution appearing to be rapid with recovery rates consistent and high indicating that contrary to earlier expectations the large 667g tablets were uniform in composition throughout. The successful application of this product eliminated the need to source Al-10%Ti rod, a product which was expected to be the most likely successful candidate.

When the decision was made to include boron as a variable it was known that the only suitable form in which to add this element without simultaneous addition of titanium was via master of the AlB_2 type. "In-house" production of a boron master alloy was ruled out due to the documented[48] complexity of the issue and an inability to analytically differentiate between the AlB_2 and AlB_{12} structures. AlB_2 master alloys are not commonly encountered therefore explicit requests were made to an agent of a company known to produce master alloys of the correct form (Kawecki-Billiton). Responses from this agency indicated that the request had been forwarded to the producer. The requested Al-3%B master alloy was used in some trial castings and produced excellent grain refinement and noticeably increased porosity. Even though the results produced in Section 4.3 indicated

that boron losses during degassing could be appreciable, this element was introduced prior to degassing in a deliberate attempt to minimise anticipated porosity increases. This procedure was supported by the 1992 comments of Eckert[125], who stated that the use of boron compounds was *"restricted to non-hydrogen sensitive applications or where effective subsequent degassing can be accomplished."* The recovery rates achieved with boron addition were approximately half those experienced with titanium, no doubt as a result of the effects of degassing.

Several of the intermediate titanium/boron ratios were deliberately selected so as to allow the use of commercial 5%Ti-1%B master alloy. The "5:1" master alloy was in rod form and is reported as capable of achieving full refinement within periods as short as one minute.[67] When using the "5:1" master alloy some compromise was required regarding the compositions achieved, as variation in recovery rates between titanium and boron had been overlooked during the experimental design. When titanium/boron permutations were required which could not be achieved by addition of "5:1" alone, supplements of the appropriate amount of either titanium compacted powder or boron master alloy were made.

Boron Master Alloy Complications

Following completion of the cast sample production, for reasons of personal interest more than necessity, an evening was spent preparing and micrographically examining specimens of an Al-4%B (AlB_{12}) and the Al-3%B (AlB_2) master alloy. No information could be found regarding the appearance of the respective microstructures however surprisingly, no obvious differences could be seen between the two structures. Physical testing of the cast specimens (see Chapter 6) conducted concurrent with final sample production revealed no anomalies to suggest that the 3% boron alloy was anything other than the AlB_2 requested.

To eliminate doubts regarding the 3%B alloy, samples of both the 3% and 4% boron alloys were sent to the NZAS laboratories where XRD analysis was carried out. The results of this testing were not conclusive but did confirm the presence of AlB_{12} within the 3% alloy while AlB_2 could not be detected. Since all casting had been completed it was too late to suspend use of the now questionable boron master alloy. To definitively assess the nature of this alloy samples of both the 3% and 4% boron alloys were then sent to the Research

and Development Section of Kawecki-Billiton Metaalindustrie BV (KBM) (the master alloy producers). Suspicions that both alloys were of the AlB_{12} type were soon confirmed, hence, *DESPITE DELIBERATE EFFORTS TO UTILISE A BORON ALLOY OF THE AlB_2 TYPE, THE BORON MASTER ALLOY USED IN THIS RESEARCH WAS OF THE AlB_{12} TYPE.*

Metallographic images of AlB_2 and AlB_{12} type master alloy samples provided by KBM are shown in Plates 7 and 8. Hopefully these clearly different microstructures may allow other researchers to rapidly differentiate between the types of boron master alloy available and hence avoid the anguish of using an inappropriate product.

5.3 CHEMICAL ANALYSIS

With the exception of phosphorus, all chemical analysis was performed by optical emission spectroscopy at NZAS Ltd. The full range of 21 elements monitored are indicated in the analysis ranges listed below, while tables of the full analysis results from the 495 cast specimens are listed in Appendix H. The spectrometer used was an Applied Research Laboratories (ARL) 3460. The detection and calibration ranges for this analyser are listed below (from ARL brochures and NZAS). Unfortunately no information regarding the precision of output results has been made available.

	Guaranteed Machine Detection Limit (ppm)	*Calibration Upper Limit (%)*		*Guaranteed Machine Detection Limit (ppm)*	*Calibration Upper Limit (%)*
Si	1	34.2049	Ca	0.2	0.0615
Fe	2	3.1500	Na	0.4	0.0310*
Cu	0.5	12.6057	V	0.5	0.0487
Mg	0.4	10.8953	Ga	0.2	0.0365
Zn	3	11.1299	B	0.4	0.0298*
Ni	0.7	0.2468	Li	0.01	0.0317
Mn	1	1.4486	Be	0.005	0.0117
Pb	0.8	0.0792	Bi	1	0.0433
Cr	0.4	0.5828	Zr	0.2	0.2842
Ti	0.5	0.3078	Sr	0.1	0.0834
Sn	2	0.1824			

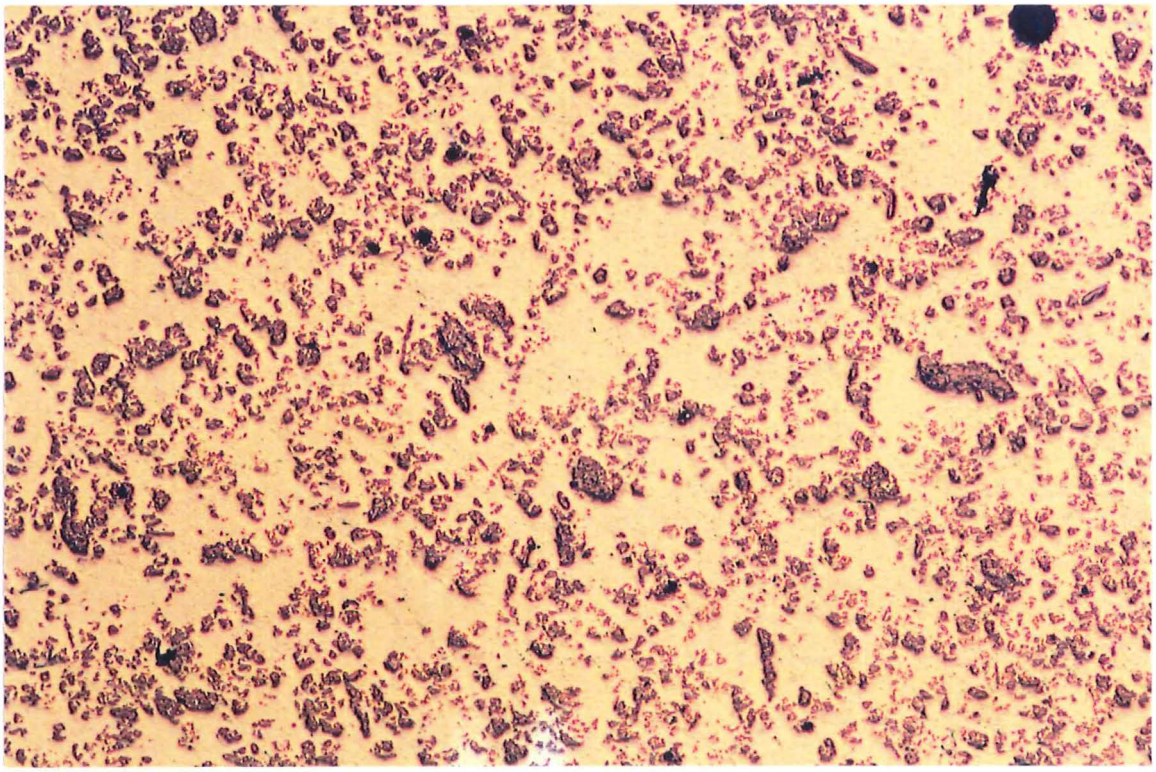


Plate 7: The AlB_2 microstructure of a 3%-boron master alloy (x57).

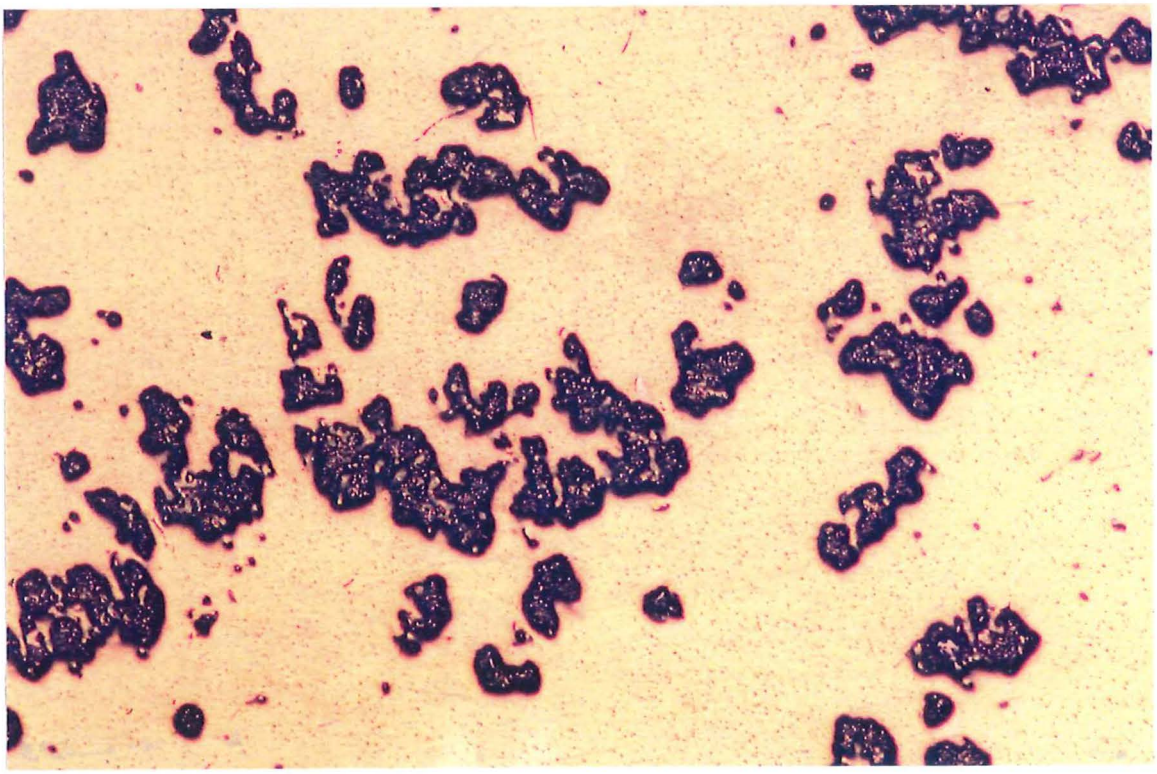


Plate 8: The AlB_{12} microstructure of a 4%-boron master alloy (x57).

From the above data it can be seen that the calibration limits for both boron and sodium(*) are somewhat lower than that of some of the samples produced. The number of samples affected by this problem was relatively small and the predicted error introduced was thought to be no higher than would have been experienced using alternative analysis techniques. The quoted calibration ranges supplied by NZAS Ltd are thought to be conservative since copper contents well beyond the scope of the above range were analysed with complete accuracy during production of Al-Cu master alloys for other work.

5.4 MOULD DESIGNS AND TEST PIECE SECTIONING

Spectrochemical Analysis Discs

One spectrochemical analysis disc was cast, in accordance with the practices outlined in ASTM E716[3], for each sample pour which took place. A preheated centre-pour permanent-type mould was used as described by the ASTM standards. Each cast disc had the central sprue removed, was identified and then dispatched to the NZAS laboratories for machining and spark analysis.

Physical and Structural Analysis Samples

The physical and structural property samples used to measure strength, ductility, grain size, porosity, etc were all obtained from sections of a single sand-cast test bar produced for each composition. The moulds used were all obtained from a local commercial foundry. They were formed in cold-setting resin-bonded sand, had an external diameter of 102 mm and internal dimensions that complied with the recommendations laid out in BS1490. The form of the final castings and the positions from which test specimens were cut are illustrated in Figure 35.

In order to monitor variables in regions as close as possible to the tensile test specimens, hardness, modification and porosity measurements were conducted on the lower surface of the small specimens, as shown in Figure 35. The majority of grain size analyses were carried out on the lower surface for similar reasons, however in order to assess some

difficult structures both top and bottom surfaces were examined. The large feeder head from each specimen has been labelled and retained in the hope that at a later date, further analysis (particularly phosphorus analysis) may take place and more fully utilise the data already recorded (see Section 11.1).

Straube-Pfeiffer Samples

Straube-Pfeiffer (RPT) tests were performed on several compositions, however maintaining consistent vacuum conditions from one test to the next proved difficult with the equipment at hand. Since the results of Straube-Pfeiffer testing were of secondary importance, this line of analysis was not pursued for all casts. Those samples which were tested were cast in a steel tapered-cup mould of approximately 65mm depth and top and bottom diameters of 50mm and 30mm respectively. Each cast specimen was sectioned down the centre so as to reveal the degree of internal porosity. It was soon realised that porosity variation between vacuum cast samples bore little relationship to the porosity evident in specimens cast at atmospheric pressure. Consequently these results were considered of marginal significance and no record, qualitative or otherwise, was kept.

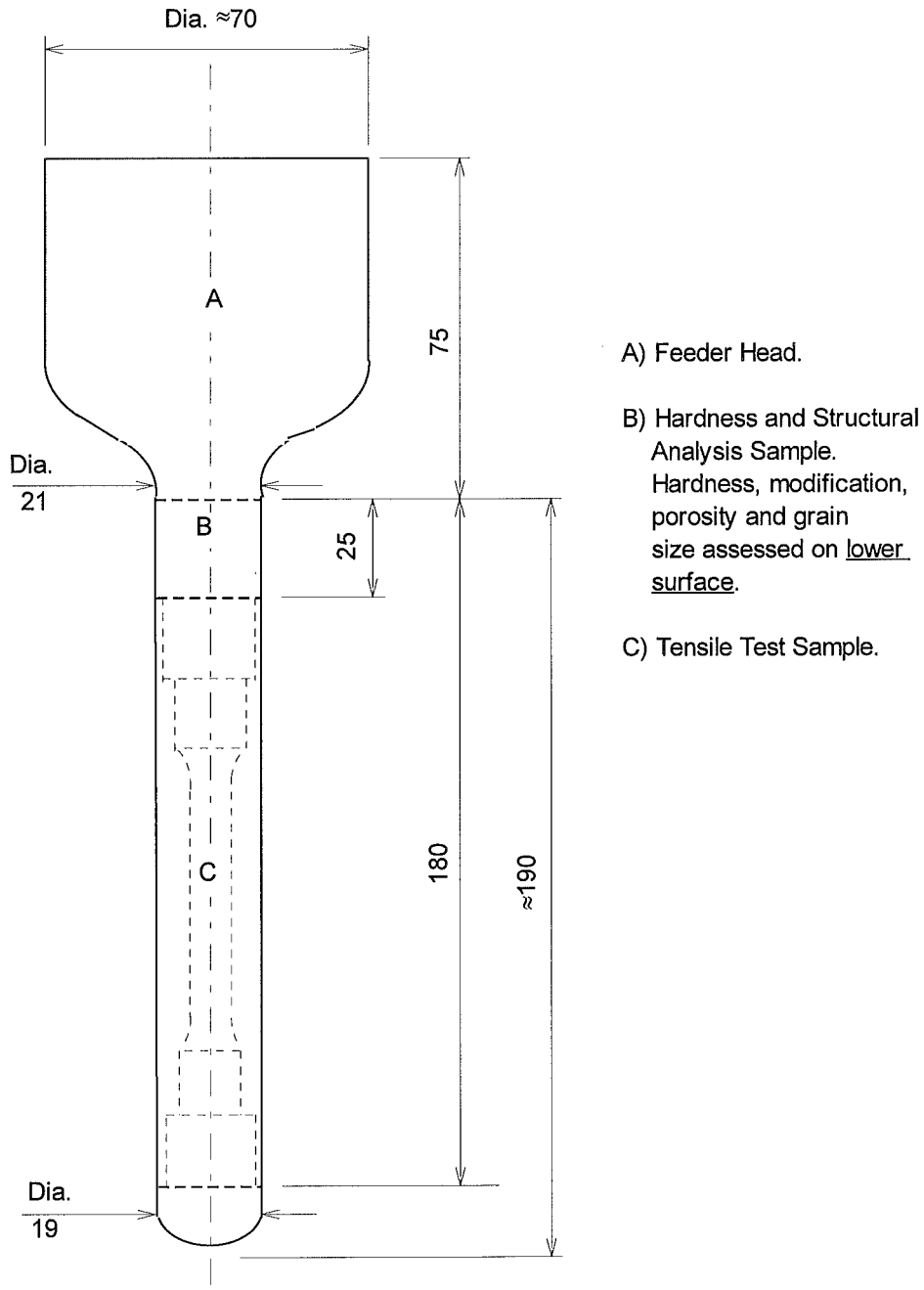


Figure 35: Casting format of the physical and structural analysis samples

5.5 FOUNDRY OBSERVATIONS

Oxide Layer Variation with Modification

As mentioned by Mondolfo[78F] and Gruzleski[18V], several reports have been made of sodium additions reducing cast fluidity. Work by Argo and Gruzleski[157] has shown that any fluidity variation, should it exist, is exceedingly hard to quantify. During this study it became obvious that as sodium levels increased, melt oxide layers formed faster and became substantially thicker. This propensity to form thick, tenacious oxide layers was obvious, even at low sodium levels (<0.01%) and caused high sodium samples to routinely display entrained oxide layers on cast surfaces. No attempt was made to quantitatively measure fluidity or oxide variation but it is conceivable that earlier observations regarding decreased fluidity may primarily be a result of oxide films dominating casting characteristics rather than a variation in the fluidity of the underlying liquid.

While strontium also increased the speed and thickness of oxide formation, this effect was far less pronounced than that observed with sodium. Increased oxide layers due to strontium addition only became noticeable when levels exceeded ≈0.04%.

Tool and Crucible Degradation

Regularly recoating the steel foundry tools with alumina refractory paste was not sufficient to completely avoid tool degradation. At the completion of casting material loss was evident on both the plunger and scraper used. The amount lost was minimal considering that 270 melts had been conducted. The graphite lances also evanesced, so much so that they were replaced after producing approximately 190-200 samples. Degradation of the lances was due to both the regular abrasive cleaning required prior to recoating with alumina paste and also to breakdown within the melt, the effects of the former were considered to be more prevalent. Although loss of material from the lance was apparent during processing no carbon particles were observed in any microstructures.

Crucible life was found to be limited, with crucibles seldom remaining serviceable for more than ≈ 45 melts. Most crucibles were removed from service once large sections of

their outer surface began to spall away from the core. This failure was associated with direct exposure to the furnace flame and thermal cycling rather than exposure to molten alloy. As with the graphite lances, the crucibles suffered appreciable erosion due to the nature in which the spent refractory paste was removed. On the few occasions when the refractory layer was breached by molten metal, removal of the subsequent melt residue resulted in a substantial reduction in wall thickness. Under the conditions of this research, alumina-coating the crucibles proved very worthwhile. (In situations where such stringent residue removal is unnecessary,. i.e. commercial applications, no clear conclusions on the worth of the process could be drawn.)

Sand Mould Preparation

Prior to being used, the sand moulds were stored in the production foundry; this provided a dry, heated environment. In order to remove all traces of moisture and prevent porosity, the initial moulds used were calcined in a small, low-temperature furnace before use. This practice was halted after the 47th melt as no noticeable change in porosity, or any other casting property, was detected when calcining was omitted.

6.0 PHYSICAL TESTING PROCEDURES

6.1 MODIFICATION LEVEL

As mentioned throughout Section 2.2, the modification of eutectic silicon is often inhomogeneous, even on a microscopic scale and consequently, the method used for quantifying the degree of silicon refinement must take into account the relative amount of each modification level present (see Plate 9). Possible methods available for quantifying modification level include visual comparison with set standards, image analysis and monitoring physical properties which are influenced directly by chemical modification, e.g. thermal analysis. Image analysis has major flaws with regard to quantifying modification states. Firstly, several images of each sample would require analysis and secondly, this process of quantifying silicon particle size and distribution is unable to differentiate between over- and under-modified states. Thermal analysis is not sensitive enough to yield useful quantitative results, especially given the compositional variation among the test samples. By virtue of these points, visual comparison with set standards was deemed the only feasible technique for the analysis of the 495 test samples.

Variability in modification levels is not only due to local variations in composition but also local cooling rates, therefore one section of a casting may have substantially different silicon morphologies than a section of the same casting subject to different cooling conditions. In an attempt to minimise this effect on the test-bar results, all modification levels were assessed from sections through the same position on the cast test-bars, as shown in Figure 35. The cross-sectional area of this region is quite small. A larger area could have been analysed using the casting head region or by casting separate samples specifically for modification analysis. The former would have necessitated the quantification of modification in a region subject to slower cooling than the tensile test piece, thus making comparison between the modification level and mechanical properties difficult. Separate modification samples were not pursued as this would cause the same problems as just mentioned and any foundries wishing to apply the results of this research

would be required to adopt the practice of casting similar, dedicated, modification analysis castings (something considered unlikely).

In order to observe the modification characteristics of each cast specimen, sections through the samples were first machined and polished to a 1μm diamond finish. The microstructural constituents, including the eutectic silicon, were then examined by optical microscope. To obtain the photomicrographs contained throughout this report, certain samples were subject to final polishing with ¼ μm diamond and then etched in a 0.5% HF solution. Several etchants were investigated (as listed in Appendix G) yet none proved significantly better in any regard than 0.5% HF. The identities of the phases indicated in the various photomicrographs were established using an energy dispersive X-ray analyser in a scanning electron microscope and/or the illustrations and descriptions provided in references 78, 133, 144, 158, 159, 160 and 161.

The modification rating for each sample was established using standard AFS (American Foundrymen's Society) modification scales[162]. This scale consists of six microstructures labelled from 1 to 6, with 1 representing a coarse unmodified structure through to six representing a very fine fibrous eutectic. Each scale value was multiplied by the proportion of the sample area which it represented. For example, if 20% of a sample microstructure is rated 2, 65% rated 3 and 15% rated 4 then the modification rating is given by:

$$(0.2 \times 2) + (0.65 \times 3) + (0.15 \times 4) = 2.95.$$

This analysis method is outlined by Closset and Gruzleski[18W]. As only a small area of the sample cross-section could be viewed at any one time, the entire section was first scanned and then three separate "typical" micro-regions, regarded as representative of the whole section, were selected for analysis. In an attempt to gauge the level of modification inhomogeneity, and the suitability of analysing a single cross-section, six samples were sectioned five times at positions some 2-3mm apart. These six samples were selected so as to represent a range of both modification and porosity levels. The variation in modification rating, from cross-section to cross-section, within a single sample never varied by more than ± 0.5 an AFS unit. This level of variation was only encountered in two samples, each of which displayed partial modification and severe segregation of the modified and

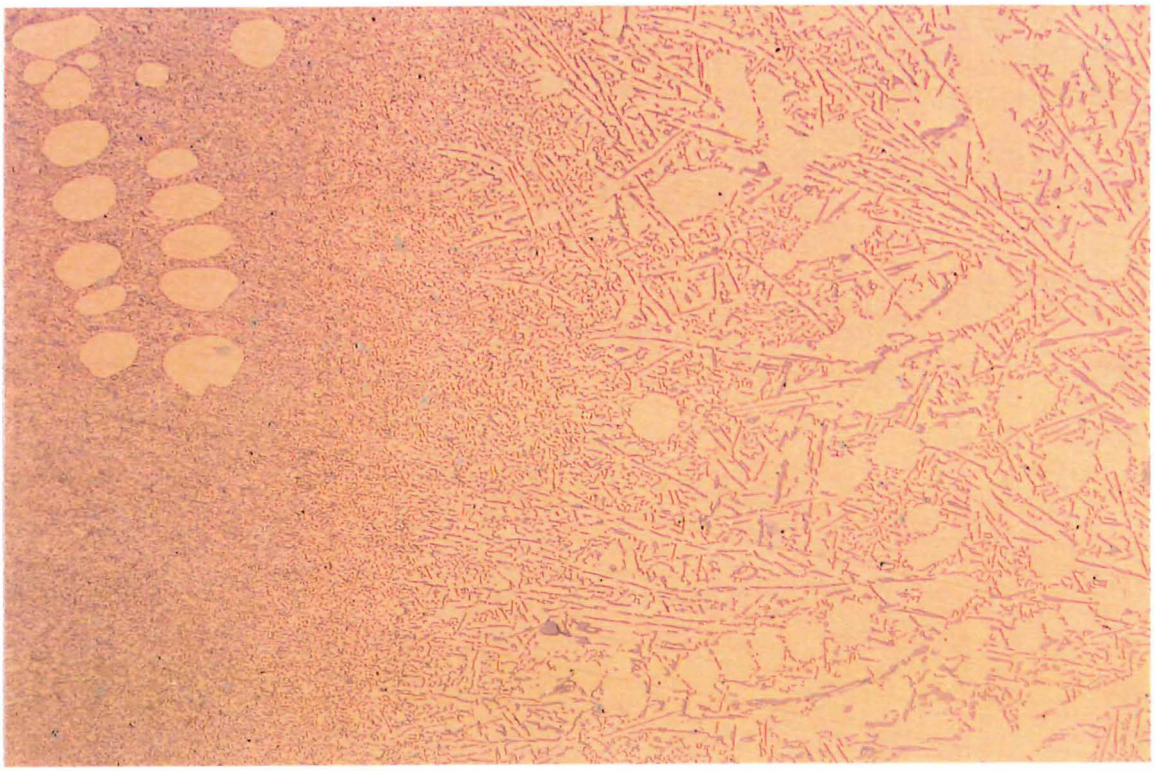


Plate 9: An example of the heterogeneous modification states present within a single microstructural region, sample 236-1-146 (x114).

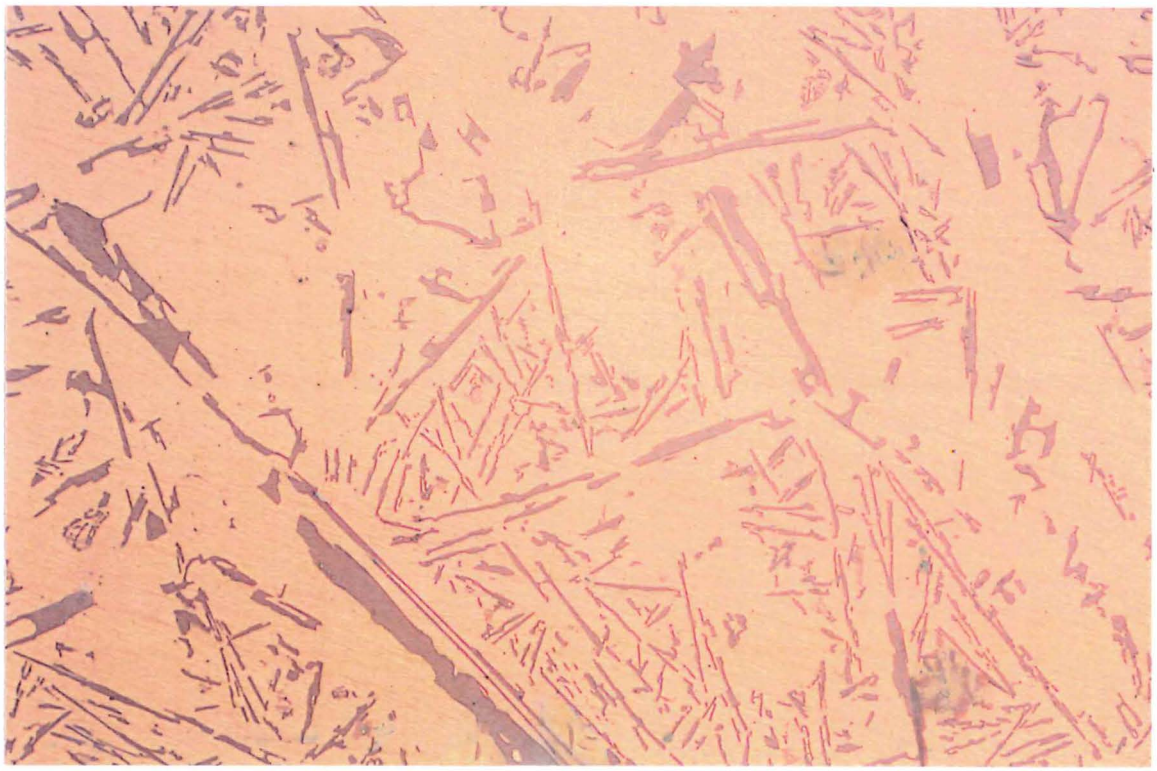


Plate 10: An example of a microstructure containing regions given the modification rating of zero, sample 29-3-79 (x220).

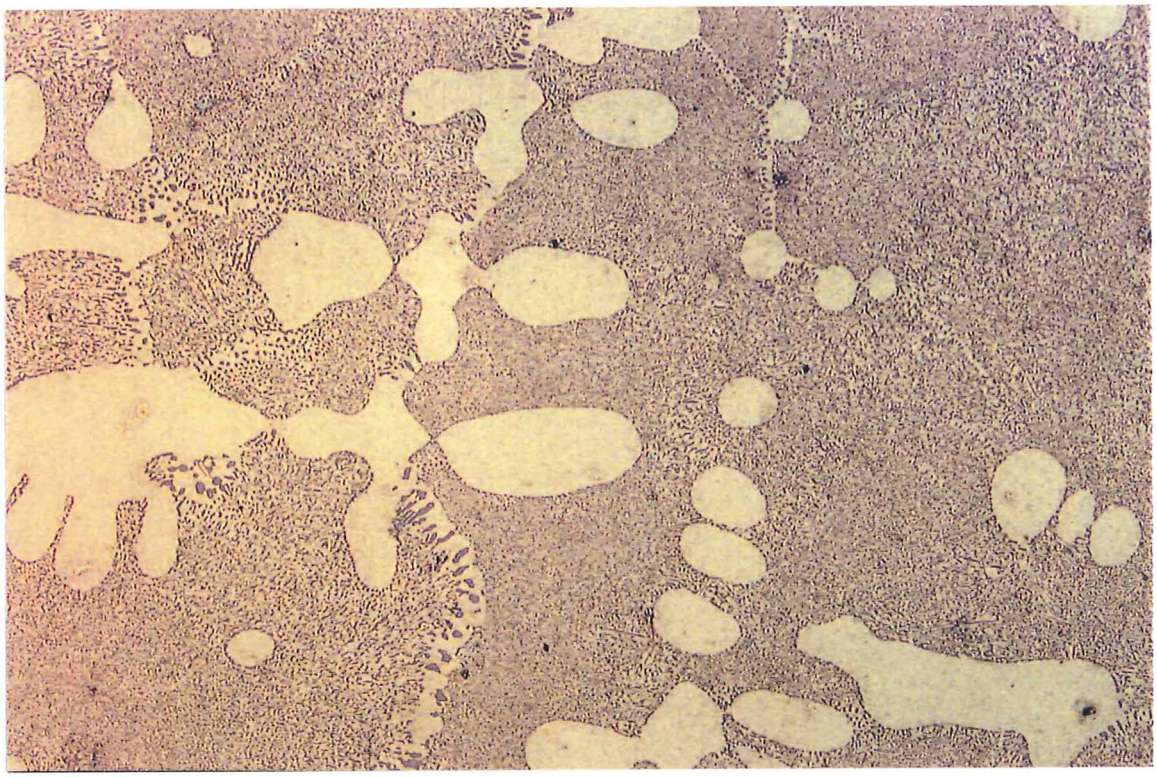


Plate 11: An example of a microstructural region given the modification rating of seven, sample 176-2-114 (x110).

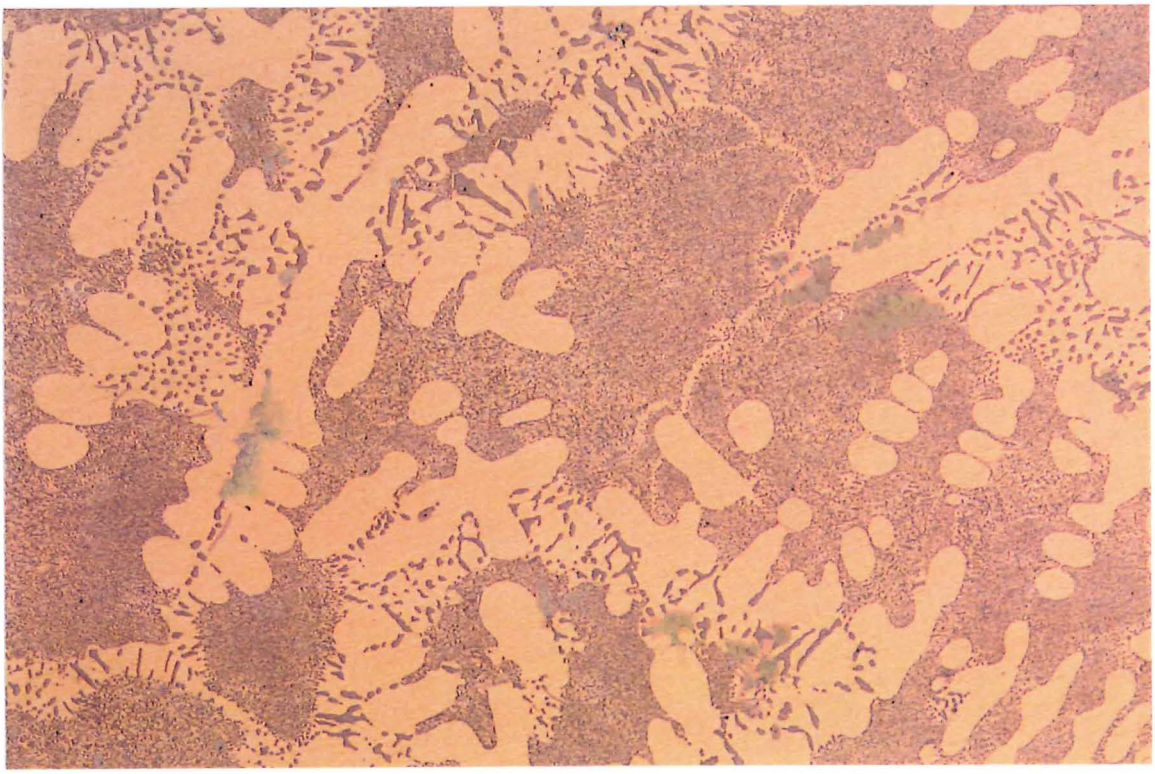


Plate 12: An example of a microstructural region given the modification rating of eight, sample 176-2-114 (x114).

unmodified structures. The full set of tabulated results from the final test piece sections are contained in Appendix I.

One problem encountered when using the AFS silicon refinement scale was that it stops at a rating of six, corresponding to an ultra-fine fibrous structure; this leaves the question of what to do with overmodified structures. Two options were considered: to rate the overmodified structure as equal to an undermodified structure displaying a similar degree of coarseness (but different silicon shape) or to set up further standards relating to overmodified and grossly overmodified structures. Each of these options has associated problems. However, to allow clear distinction between over- and under-modification in future MLR predictions, the latter system was selected with additional scales rated seven and eight. At the coarse unmodified end of the scale, an additional level of zero was also established thus enhancing identification of a very coarse acicular structure encountered within regions of some high-silicon unmodified structures. Even in the presence of phosphorus, it is doubtful that the zero level would be required in alloys containing less than 10% silicon.

Samples displaying regions rated as zero, seven and eight are shown in Plates 10,11 and 12.

Since the AFS modification number of six represents a very fine "super modification" state which was observed in very few samples, any samples reported as having an overall rating of six can be assumed to have displayed small regions of overmodification. As a result of this the optimal modification rating can be assumed to be approximately five and a half. (The strontium modified samples generally did not display refinement to this rating irrespective of the modifier addition level.)

6.2 POROSITY

Porosity can be measured by a number of techniques, most of which were discussed in Section 2.4. The established quantitative methods for directly assessing porosity include density tests and the sectioning of atmospherically or vacuum cast samples. It should be remembered that while hydrogen levels are instrumental in the formation of porosity, measurement of either porosity or hydrogen level cannot be used as a quantitative measure of the other. Thus, hydrogen measurement techniques cannot be used as a complete means to assess porosity levels.

Initially it was hoped to use density tests as a measure of porosity. However, this possibility was complicated by the need for density compensation due to changes in composition. In atmospherically cast samples, the variations in density due to these changes were predicted to be of the same magnitude as those due to the anticipated porosity. This problem could have been alleviated by the use of vacuum solidification and compensating for the theoretical density of each sample. Vacuum processing would have necessitated the design and development of special vacuum equipment and ideally the use of specially designed moulds such as those described by Sulinski and Lipson[102]. The theoretical density calculations would have been compromised by errors within the composition analysis data as well as any errors present within the available tabulated density charts. These problems were surmountable but this form of analysis was not pursued due to the findings of both Herrera and Kondic[100] and Surappa et al[116], who found that physical properties are more strongly related to measured porosity area than to sample density.

As pore formation is dependent on the feeding and cooling characteristics of the alloy in question, porosity levels are far from homogeneous throughout a casting. This means that the area of porosity displayed in a given cross-section will be dependent on the position in the casting from where the section was taken. For the same reasons as those given for modification sampling, porosity sections should be taken from a constant position on the test-bar castings, thus the section employed for quantifying the modification level was also used to monitor porosity. The polishing required to assess modification (down to 1μm

diamond) was sufficient to reveal exceedingly fine pores. Attempts were made to assess the area of porosity present in each section using a Flinders Imaging MD20 image analyser. Direct images of the polished samples were not adequate as the contrast between the pores and the polished surface was insufficient to permit each pore to be clearly distinguished by the image analyser. Direct editing of images of this type on the analyser screen proved difficult and of dubious accuracy and thus was not pursued. In an attempt to increase the contrast between pores and the polished surface, various fillers were deposited into the sample voids. This process proved unsuitable as repolishing was often required whence the fillers tended to dislodge, particularly from very fine pores. Success was only achieved by photographing individual samples then manually shading the regions occupied by pores. Analysing images of each complete sample cross-section, created by the above process, revealed that if each image was processed only once then accuracy was compromised by the resolution of the system. This was a major setback as the time required for photographing, editing and then repeatedly analysing 495 sample images was not available.

Due to these problems, six easily distinguished reference samples were visually selected. The reference samples ranged over the entire porosity spectrum encountered, from nil to slightly over 1% porosity by area and are shown in Plates 13-18. To ascertain the validity of using these empirical reference scales, enlarged images of each standard section were processed several times via manual correction of detected pore regions. This gave the following results:

Reference Scale	*Image Analyser Pore Area (Reference Levels)*
1	0.00%
2	0.05%
3	0.19%
4	0.41%
5	0.61%
6	1.07%

Plotting these areas versus their empirical rating revealed a good fit to a quadratic function, i.e. the optical rating is proportional to the square root of the actual porosity area (see Figure 36). This implies that the lower the porosity area, the more sensitive this visual differentiation scale becomes. This was highly desirable as most samples contained less than 0.4% porosity.

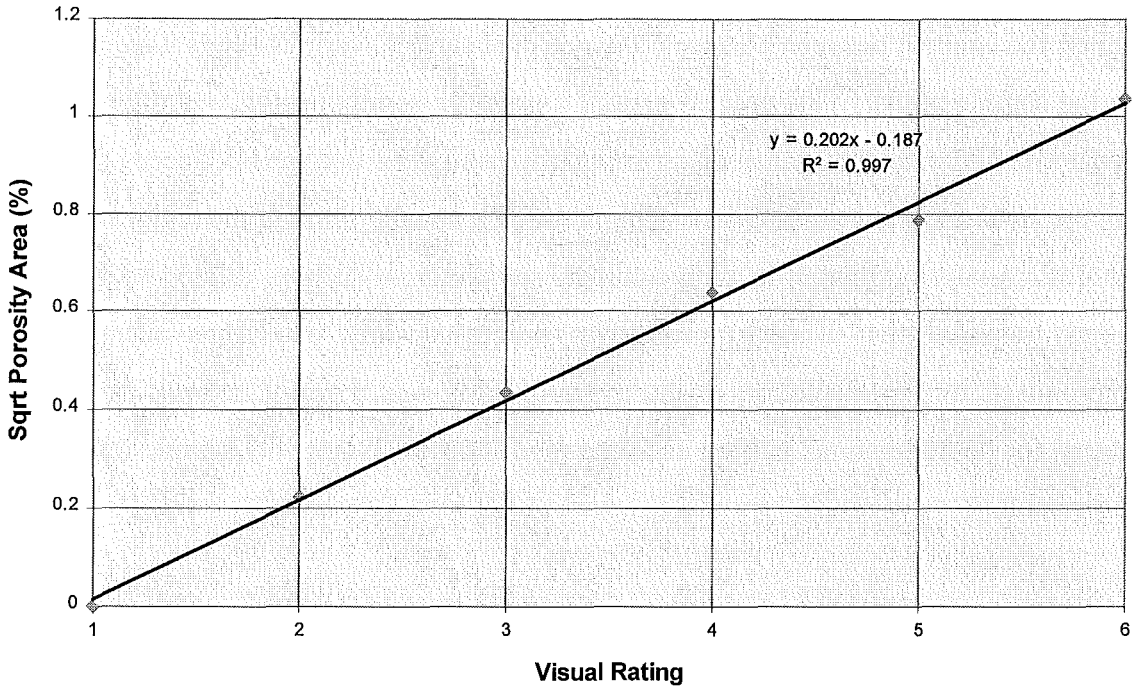


Figure 36: Porosity standard characteristics.

The dependence of observed porosity on the cross-section viewed was investigated in the same manner and concurrent with that detailed for modification (see Section 6.1), i.e. six samples were sectioned five times each. The only set of ratings found to display an appreciable variation originated from a sample displaying a high level of porosity in the form of a few large voids. As result of this, the few samples (>10 from the 495 produced) which displayed this form of porosity were rated on both their top and bottom surfaces and the mean value taken.

The remaining samples were analysed by direct comparison with the above standards. Each sample was rated three times to the nearest half scale and the results averaged and converted back to porosity area using the relationship mentioned above. The final porosity results are displayed in Appendix J.

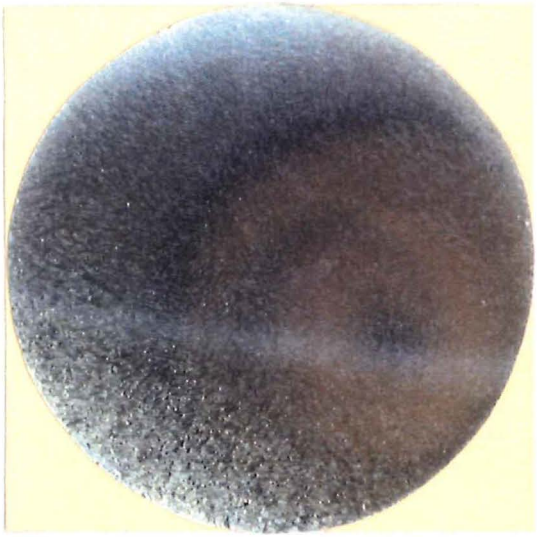


Figure 13: Porosity reference sample 'one', 0.006% porosity by area (x3).

Figure 14: Porosity reference sample 'two', 0.05% porosity by area (x3).

Figure 15: Porosity reference sample 'three', 0.19% porosity by area (x3).

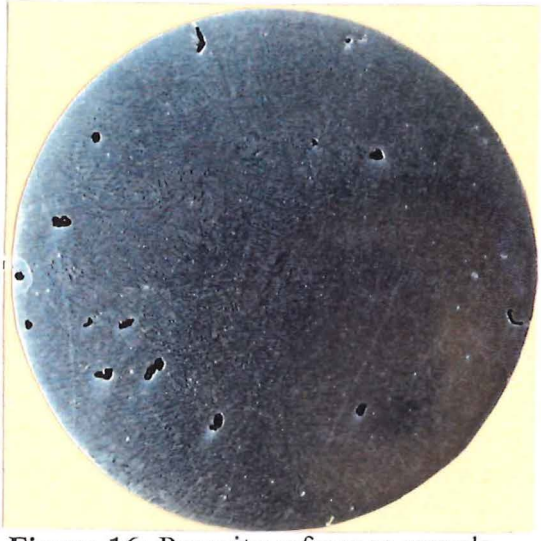


Figure 16: Porosity reference sample 'four', 0.41% porosity by area (x3).

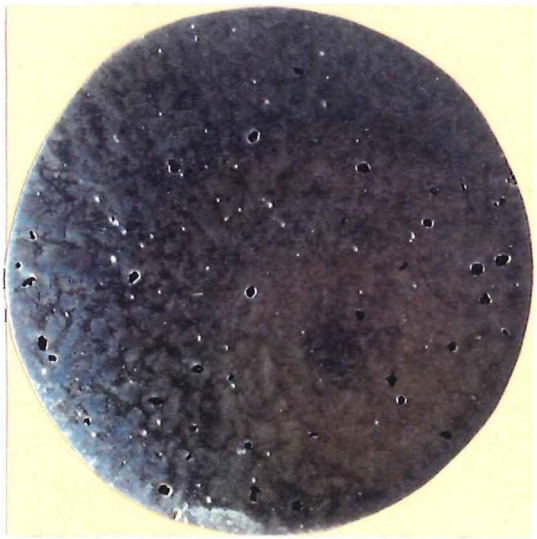


Figure 17: Porosity reference sample 'five', 0.61% porosity by area (x3).

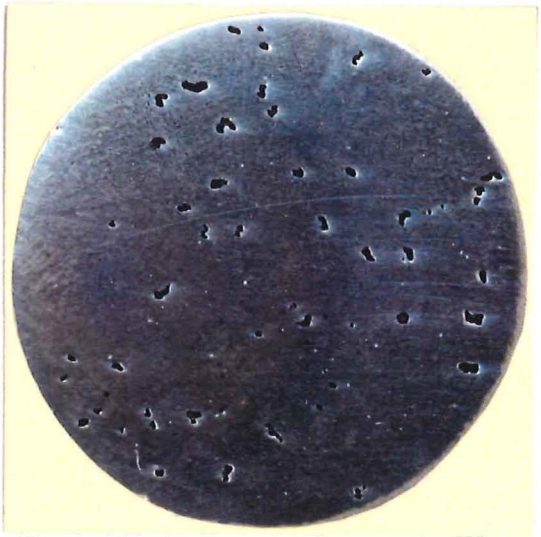


Figure 18: Porosity reference sample 'six', 1.07% porosity by area (x3).

6.3 HARDNESS TESTING

Using the same samples as used for quantifying modification and porosity, hardness testing was conducted via a Vickers Hardness machine with a 10kg test load. This testing was performed in accordance with the specifications laid out in BS427:1990[163] and AS1817:1991[164]. Testing trial samples revealed that the hardness varied significantly from region to region on single cross-sections. In order to compensate for this inherent variability, a series of tests were performed in a traverse across the centre of each sample. Using the specified three indent-diameter spacing from the sample edge and six diameters between tests it was possible to perform six indentations per traverse, as shown in Figure 37. The full results, along with the average and standard deviation per sample, are contained in Appendix K. As can be seen in the recorded results, several samples were significantly harder in the centre than at the edge, whilst others displayed exactly the opposite. Of the several possible causes of these trends, e.g. pure eutectic regions, impurity densities, etc, none may be readily detected via simple compositional data. The most promising way to isolate the factors responsible for the observed hardness variations would involve extensive metallography something which, to date, has not been pursued.

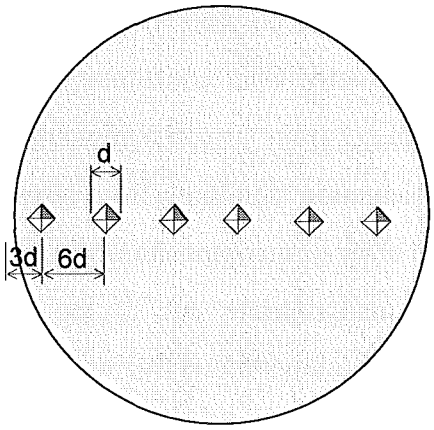


Figure 37: Hardness Indent Positions.

6.4 GRAIN SIZE

6.4.1 What Constitutes a Grain?

Before it becomes possible to quantify the grain size of Al-Si eutectic alloys it is necessary to define exactly what constitutes a grain. In alloys containing predominantly primary aluminium, a "grain" is conventionally regarded as the region occupied by aluminium of a single orientation stemming from growth of a aluminium dendrite from a single nucleus. When an alloy of a composition which is close to a eutectic is encountered, this definition becomes inappropriate due to the large proportion of mixed eutectic phase. With hypereutectic alloys the above definition loses all significance as no primary aluminium exists. In the case of hypereutectic Al-Si alloys, primary silicon solidifies as faceted, unconnected blocks in a matrix of eutectic colonies. Within the BS1490 LM6 composition range, primary silicon can only represent a very minor proportion of the structure so properties of hypereutectic alloys of this type are governed by the form of the eutectic. The issue of eutectic solidification and colony formation was dealt with in section 2.1. However in general, when a eutectic forms in a liquid made up of several elements it does so in a manner very similar to that of a single phase, i.e. dendrites grow from a nucleus.

In this study a grain has been defined as the region occupied by primary aluminium of a single orientation or the region occupied by a single eutectic colony.

6.4.2 Revealing Grain Boundaries

Several processes were tried in an attempt to satisfactorily reveal the grain structure of the cast Al-Si samples. The methods tried included the use of: several etchants; anodising; polarised light and varying incident light angles and colours. Whereas in low silicon and wrought aluminium alloys[165] etching produces contrasting grain boundary regions, in the eutectic alloy all of the methods investigated distinguished entire grains by changing the colour or shade of each grain region. A result of this was that no image was produced which could be directly resolved and analysed by the computerised image analysis equipment available.

In certain instances anodising can be used to reveal individual grain regions, as the anodic films have bi-refringent qualities which are dependent on the orientation of the grain upon which they are deposited. When a suitably anodised sample is viewed under polarised or cross-polarised light, individual grains appear in varying shades or colours. Some early reports of this technique, developed in the 1940s, suggested that the grain structure of all common aluminium alloys could be successfully revealed[166], while others concede that neither Al-12%Si nor Al-10%Mg type alloys will respond to this process[167]. Given the general lack of information available on this subject and the ready availability of anodising equipment some basic experiments were performed. Several samples, either unetched or lightly etched in 10%HF or Poultons etch, were anodised for varying times in a miniaturised commercial sulphuric acid anodising bath (floroboric acid (HBF_4) anodising solutions are more typically used for grain exposure). Each sample was then viewed under polarised light; none displayed appreciably enhanced grain definition so this simple anodising process proved of no real advantage.

Several macro-etchants were tried with mixed results. Appendix G lists the etchants investigated and summarises the experimental findings. Some of the etched structures produced were viewed under cross-polarised light; none displayed the colouring expected when viewed in this manner. The most successful etchants for accentuating the separate regions within both primary aluminium and eutectic colonies proved to be Poultons etch, $CuCl_2$ in water and $FeCl_3$ in water. Poultons etch is made up of 95% concentrated nitric, hydrochloric and hydrofluoric acids and consequently, it is exceedingly potent and dangerous to handle. While this etch produced good results it offered no real advantages over the two other successful solutions - $CuCl_2$ and $FeCl_3$. Swabbing cast samples with either $CuCl_2$ or $FeCl_3$ solutions resulted in the rapid formation of thick deposits on the etched surface which were subsequently removed by immersion in concentrated nitric acid. In the case of etching with $CuCl_2$, removal of the deposited layer was accompanied by generation of obnoxious fumes, hence the $FeCl_3$ solution became the etchant of choice. The exact formula of this solution was non-critical but mostly it was mixed as 33g $FeCl_3$ crystals in 250ml water. The structure revealed by this macro-etching process contained grains of varying reflectivity dependent on the angle of incident light.

It was soon realised that projecting light of different colours from various angles would enable etched grains of differing orientation to be highlighted in a variety of colours. Examples of images generated using this technique are shown in Plate 19. This plate illustrates the degree of grain size variation which occurs within both conventionally refined and non-refined castings within the LM6 composition range. The exact method used to create these images consisted of:

- Polished test-bar sections as used for modification and porosity monitoring were etched by swabbing with $FeCl_3$ solution.
- Heavy residue remaining on the etched surface was removed by immersion in concentrated nitric acid.
- Halogen lights with red, green, yellow and blue filters, each at 90° to one-another, were projected onto the etched surfaces.
- Finally, the samples were photographed from directly above.

6.4.3 Quantifying Grain Size

Initially it was hoped to create images of the samples which could be processed by a computerised image analyser. Only one method was found to generate such images, it being prohibitively slow and expensive. The method in question involved photographing each sample several times with illumination from various angles then tracing the clearly defined grain boundaries from each photograph onto a transparent plastic overlay and so building up an image upon which only the grain boundaries were defined. Given the large number of samples to be analysed, this process was not viable and it was recognised that a comparison procedure would have to be used, such as described in ASTM Standard E112-85[168] and French Standards NF-A-04-502[169] and NF-A-04-503[170].

In order to create images in which grain sizes could be assessed using Standard ASTM-E112 grain size plates[171], each sample was colour photographed after being etched and illuminated as described above. When suitably enlarged (4.3x, 4.5x, 7.8x - depending on the grain size) most sample images could be compared directly to the ASTM Standard plates. Resulting grain numbers were then standardised to the relevant ASTM macro-grain size number using correction factors calculated by the following function:

$$Qm = 2 \log_2 M$$
$$= 6.64 \log_{10} M$$

where:

Qm = correction factor added to the apparent grain size

M = image magnification compared to full size.

For example: with 4x magnification Qm = 4, so an apparent image number of 3.5 when corrected becomes 7.5. In general, the lower the macro-grain number the coarser the grain size. It should be noted that, due to the exponential nature of the ASTM scales, macro-grain size 2 is not twice the size of macro-grain size 4.

Certain samples proved difficult to analyse by the above procedure, the main problems being due to either non-equiaxed primary aluminium or large areas of columnar eutectic colonies. Plate 20 illustrates examples of the various structures encountered, particularly those which were problematic to quantify. Sample *a* illustrates a specimen which is distinctly hypoeutectic, equiaxed and unrefined. This type of structure along with those in Plate 19, were easily assessed by direct comparison to the ASTM plates. Sample *b* illustrates decidedly columnar grains (thankfully, very few samples displayed this type of structure). Sample *c* is made up of virtually 100% columnar eutectic colonies (most colonies tended to display a columnar nature). This sample is the worst case of this type encountered and was illustrated earlier in Plates 2 and 4. Samples which were non-equiaxed, as illustrated by *b* and *c*, were analysed by the Jeffries (planimetric) method. This involved manually counting the number of grains within a prescribed area as described in ASTM-E112[168]. Almost all areas counted contained more than 50 grains, however, contrary to the ASTM recommendations (3 areas each of at least 50 grains) only a single area (a complete cross-section) of each sample was assessed. Finally, sample *d* demonstrates an equiaxed eutectic colony where the colony has grown out from a primary silicon particle. This type of growth was only encountered in the unmodified regions of samples containing in excess of 13% silicon. This is exactly what was expected (see Section 2.1); the leading phase of the eutectic has provided a primary nucleus from which eutectic growth has occurred. This type of structure was analysed by either comparative or planimetric methods, depending on the character of the surrounding regions (as with

modification, some samples were inhomogeneous, displaying both hypo- and hyper-eutectic regions). Revealing the complete grain boundary structure of two samples proved impossible; as a result they were not included in the later statistical analysis.

Most analysed cross-sections contained well in excess of 50 grains and were assessed just once. Certain samples on which grains proved difficult to distinguish were repolished and reanalysed several times; results from such samples were averaged. Inaccuracies associated with the small sample areas and performing only one analysis per specimen would be compensated for by the averaging nature of the MLR analysis technique used to process the results (see Chapter 7.0).

Following the cross-sectional analysis, several samples were sectioned longitudinally. Virtually all of these samples displayed comparable grain formations in each direction; the only exceptions were the very coarse, unrefined structures. The coarse, inhomogeneous samples were distinctly columnar in the longitudinal direction, hence samples graded with ASTM macro numbers below 7.5 may be coarser than their ratings indicate. Corrections to take this observation into account were not considered as the most likely users of the quantified results of this research are founders, who could compare the results given here with their own transverse test-bar sections.

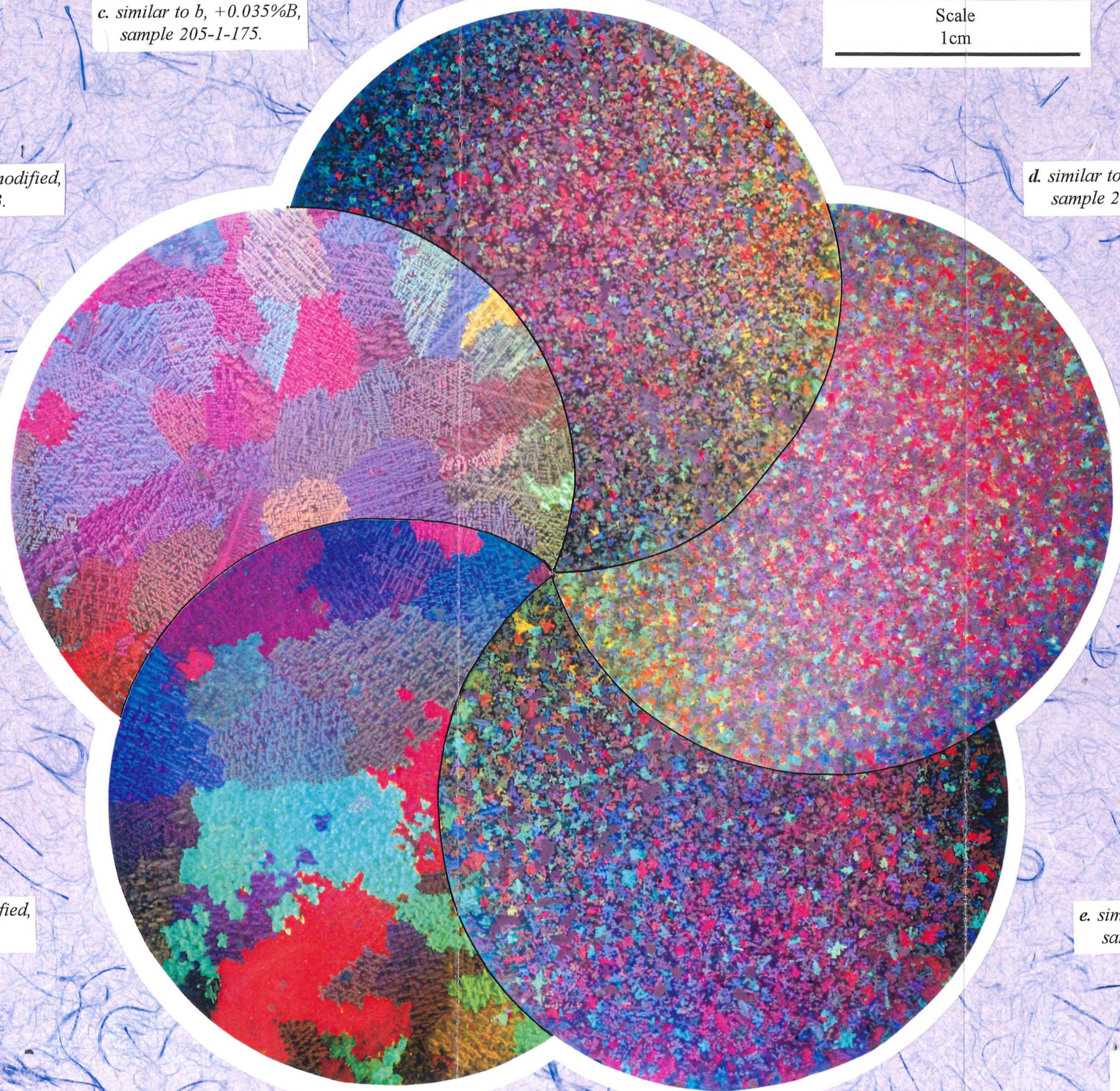
Aluminium grain boundaries within the eutectic regions (i.e. subgrains) can be revealed by etching with a modified Murakami Reagent as described by Heinz and Klemm[172]. The modified reagent was used on some cast specimens (See Appendix G.) but subgrain boundaries were not as well defined as expected; this may have been due to the degree of impurities present.

c. similar to b, +0.035%B, sample 205-1-175.

Scale
1cm

b. 10.2%Si, Na modified, sample 1-1-33.

d. similar to b, +0.048%B and 0.017%Ti, sample 260-1-260.



a. 11.2%Si, Sr modified, sample 183-4-9.

e. similar to b, +0.201%Ti, sample 33-2-67.

Plate 19: Typical refined and unrefined macrostructures.

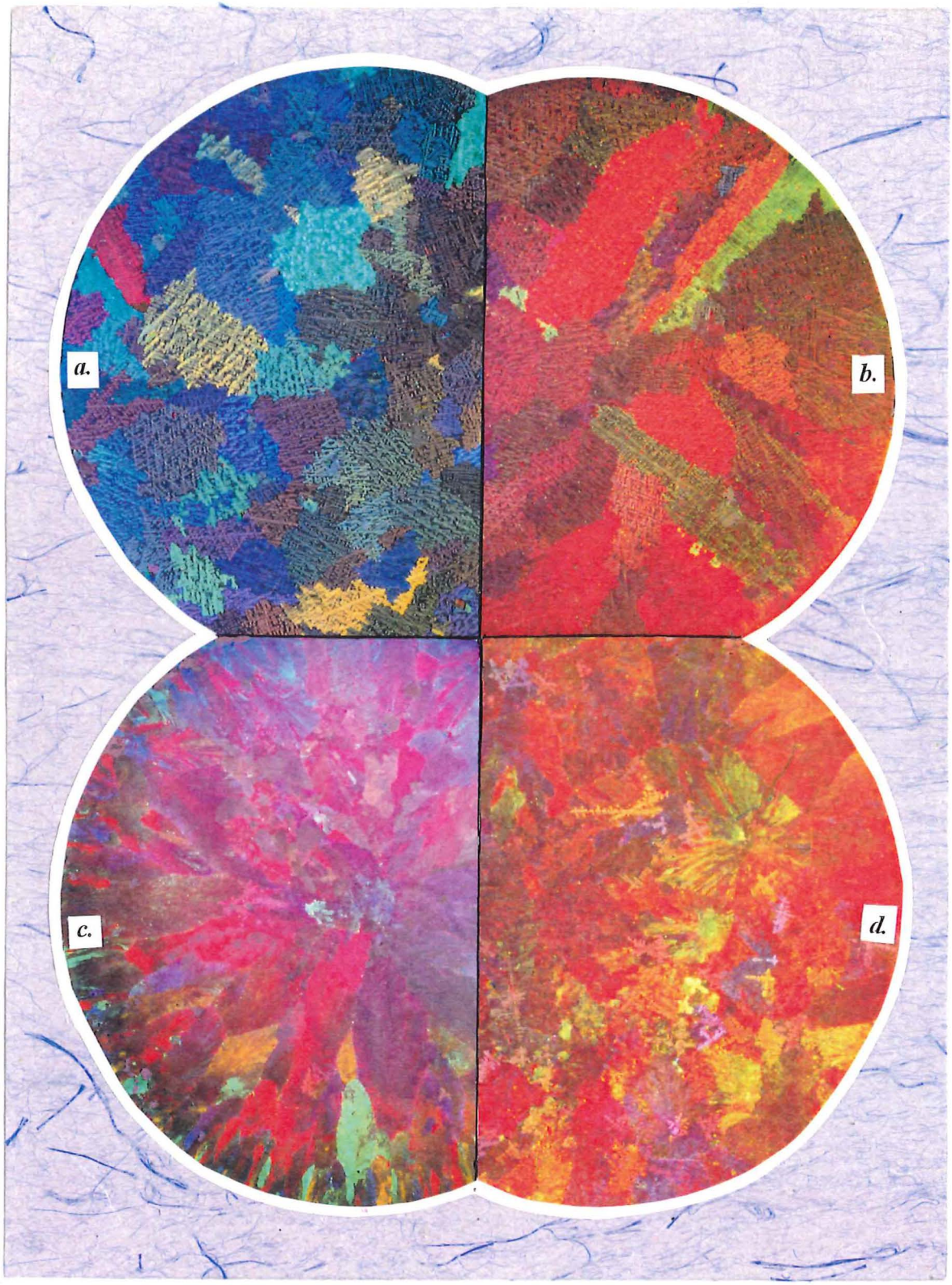


Plate 20: Macrostructures which gave problems when assessing grain size.
Samples a. 37-1-2, b. 118-1-25, c. 83-3-26, d. 81-2-26
(a-c x4.25, d x7.75).

6.5 TENSILE TESTING

One tensile test sample was machined and tested for each sand-cast alloy composition. The position in the sand mould castings from which the tensile test pieces were obtained was shown in Figure 35, while the form of the final test piece is shown in Figure 38.

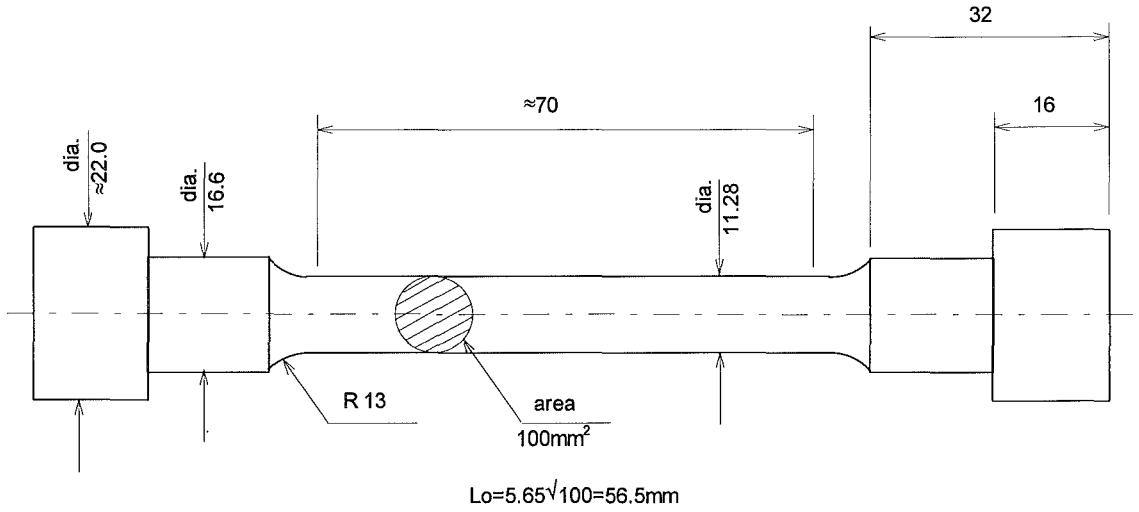


Figure 38: Tensile test sample format (all dimensions in mm).

All tensile testing was performed to the specifications set out in BS18:1987[173] on a Satec M200HVL computerised universal testing machine. The test parameters used are listed below:

- Extensometer Gauge Length 50 mm
- Stress Rate 60 MPa/min
- Elongation Gauge Length 56 mm.

The testing yielded the following information:

- Tensile Strength
- 0.2% Proof Stress
- % Elongation
- % Reduction in Area.

The full results of this testing are contained in Appendix M.

The computerised test equipment determined a value for the modulus of elasticity by analysing the first part of the stress-strain curve. However, this was seldom found to produce realistic results, so these values were not considered for further analysis. From stress-strain charts which were generated during testing it was possible to rapidly detect inconsistencies in the computer-generated data. The majority of the tensile test curves displayed a very rapid onset of plastic deformation, this minimised the influence of the "calculated" moduli of elasticity on the accurate determination of proof strength. Where the incorrect modulus of elasticity was found to be having an inimical influence on the determination of proof stress, corrected values were calculated directly from the output charts. Typical stress-strain curves are shown in Figure 39. As illustrated, iron addition caused an appreciable increase in the stress at which plastic deformation commenced.

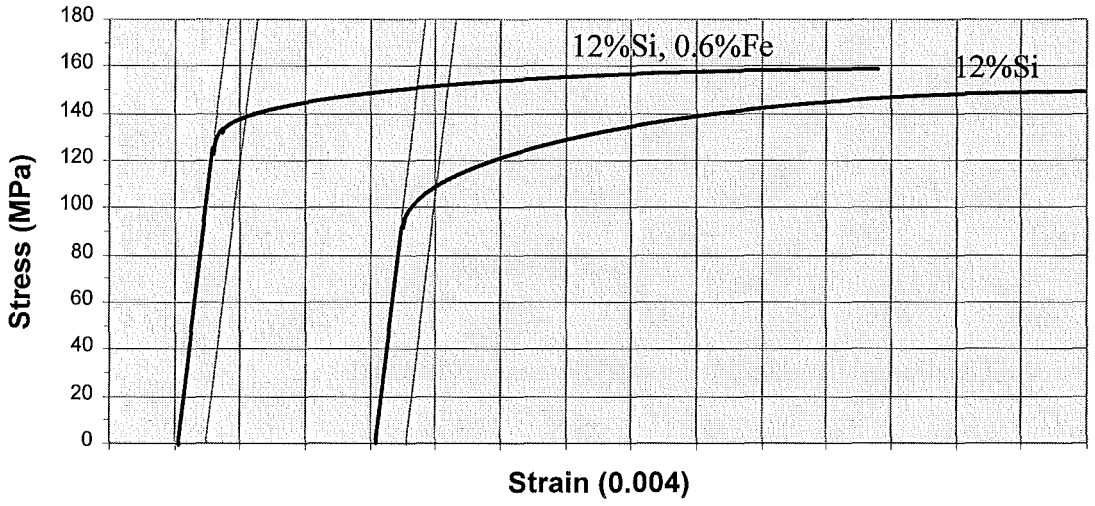


Figure 39: Typical tensile test curves (schematic)

During the course of machining the tensile test pieces, samples high in silicon were reported as being exceedingly abrasive, while those which had boron alone added as a grain refiner were prone to poor surface finish. Grinding of the parallel section of the test pieces was attempted using various grinding wheels yet no success was achieved, all wheels rapidly clogged and became ineffective. Final finishing was therefore carried out by hand using 400 grade emery paper on the rotating samples. This produced an excellent surface finish, but care was required to ensure that the diameter did not vary by more than the ±0.06mm tolerated by BS18.

The fracture surfaces of each specimen were observed, with particular attention given to samples which seemingly failed at lower loads than expected. Five samples suspected to have failed prematurely due to unduly large pores or oxides within the fracture zone were detected; these samples were later omitted from statistical analysis related to the tensile properties.

Abbreviated results of all composition, mechanical and structural analyses are contained in Appendix N.

7.0 MULTI-LINEAR REGRESSION

7.1 BASIC CONCEPTS AND APPLICATION TECHNIQUES

7.1.1 Overview

Multi-linear regression (MLR) is a statistical method used to assess the explanatory value of several different plausible predictor variables in the explanation of variation in a supposedly dependent variable. The process requires suitably large sets of recorded data from which a predictive function can be generated. Although the term MLR implies that only linear relationships may be established, this is not the case as predictor (or independent) variables can be entered into the MLR process in a non-linear form.

MLR involves simultaneously "fitting" linear relationships to several selected parameters via a complex form of least-squares fit so as to minimise errors in the prediction of the dependent variable. As the process does not require each variable to be varied independently, the number of required observations can be drastically reduced from that which would be required with conventional experimental techniques. Experimental error limits this effect, necessitating the analysis of an adequate number of observations to achieve the desired statistical significance. To fully optimise experimental design when utilising MLR, the degree of variance and error associated with each variable should ideally be known in advance. In most cases, including the present research, this is not a practical reality.

An example of the general equation that MLR solves is shown below.

$$y = k_1x_1 + k_2x_2 + k_3x_3 + \ldots\ldots k_nx_n + k + \varepsilon$$

Dependent Variable

MLR Calculated Coefficients

Independent Variables (predictors)

MLR Calculated Intercept

Error term

The first task MLR performs is to estimate the intercept k, the partial slopes k_1, k_2 ... k_n and the error variance. The arithmetic involved in MLR escalates rapidly and so must be performed by computer. In an analysis involving n independent variables there are $n + 1$ equations to solve; such equations may be solved for any number of variables and observations up to the limit of the computer's memory.

Output from the MLR process includes the calculated constant value coefficients as well as the statistical significance of each independent variable used, and the resulting equation as a whole. If all, or almost all, of the relevant factors controlling variation in the dependent variable are included within the regression analysis as independent variables of the correct form, the resulting MLR equation should have a predictive error no higher than the error due to measuring the respective properties involved. If, on the other hand, influential factors are omitted from the MLR then the predictive worth of the overall equation will be low. In this latter case it is possible that some of the independent variables may have high statistical significance so that at least the influence of these variables may be partially realised.

MLR output serves two purposes; firstly it quantifies the influence of various factors upon the dependent variable and secondly, it provides a function which can be used to predict and quantify the outcome of untested events or properties. Quantifying the influence of specific, independent parameters enables optimisation of controllable parameters in the most efficient and cost effective manner. For example, given two variables which achieve the same result, MLR will quantify the characteristics of each variable so enabling the most cost effective option to be established by informed cost analysis. Utilising overall MLR expressions for predictive purposes is possibly their most important use. MLR-based prediction allows statistically significant judgements to be made on issues which might otherwise have to be based on conjecture or expensive, time consuming and sometimes impractical, testing. An example would be the desire to know the properties throughout a large casting without physically destroying it. If prior test data is used to create an MLR expression relating independent factors such as thermal history, composition,...etc to the properties of interest, destructive testing of the final product may be avoided.

The predictive value of an MLR-derived function is most commonly indicated by an R^2 value. R^2 may be interpreted as the reduction in error achieved in prediction of the dependent variable using the derived expression as opposed to the simple mean value estimate. For example, using an MLR derived expression with an R^2 value of 0.73 corresponds to a 73% reduction in predictive error compared to that which would be achieved using the mean value of the observation data. It must be realised that the R^2 value applies only to prediction within the original data set. Should this data be non-representative of the population from which it is drawn or inconsistent with the situation for which later predictions are intended, the R^2 value becomes meaningless and generated results cannot be accurately assessed in a statistical way. Data collection for MLR purposes must be done in an unbiased manner, under conditions as close as possible to that which the final MLR results will be applied.

A full breakdown of the equations and computations used to perform MLR are well established and are employed in numerous computer packages, hence they will not be discussed here.

7.1.2 Applications, Alternatives and Potential Problems

MLR Applications

MLR analysis has found widespread acceptance in financial and commercial sectors while scientists, and particularly engineers. have been slower to adopt the process. Commercial and financial organisations employ MLR to monitor factors such as share prices, product performance, advertising efficiency and investment optimisation. Scientists employ the process to interpret the results of experimentation which has been designed so as to minimise the number of tests and observations required. The main uses engineers have for MLR are in cost estimation and optimisation of experimental procedures and results so as to assess and control processing parameters in the most effective manner. Unfortunately, engineers and scientists are seldom trained in the competent application and use of MLR, hence the process is often carried out in a limited form which severely restricts the significance of generated results (two examples of this were given in Section 2.6).

Alternatives to MLR

An alternative to MLR when several variables are being used as complex predictors of a dependent factor is the development of an Artificial Neural Network (ANN). ANNs are gaining in popularity however, they are not in widespread use and have some inherent drawbacks. Once the problems of establishing and training an ANN have been overcome, it is difficult to apply the results to anything other than prediction of the dependent variable. ANNs do not incorporate readily discernible relationships between the physical actions of the predictors and their influence on the dependent variable, hence it is difficult to learn about the process being monitored. A consequence of this is that, at this stage, ANNs cannot be used as simple methods to refine and improve processes, rather they are primarily prediction tools only. Liu et al[174] have published work which outlines the experimental development of ANNs to predict the mechanical properties of hot-rolled low carbon steel. Comparisons are made between the predictive worth of ANNs and simple first-order MLR models (see below). Each of these models utilised the same input variables and no concession was made to optimise the MLR or incorporate higher-order interactions. Not surprisingly, Liu et al concluded that ANNs provide analysis capabilities which are superior to those available using multi-linear regression. Given the basic form in which the MLR was conducted, this comparison can be disregarded and is a reflection of the ignorance which abounds on the issue of effective MLR application.

Selection of Potential Predictors

Thoughtful selection of independent variables is a prerequisite for successful MLR analysis. Collection of data and experimentation is time-consuming and expensive, hence background knowledge of the variables of interest and what influences them is a major aid in determining exactly what must be monitored and included within the MLR process. Practical "hands-on" and "shop floor" experience is invaluable when considering exactly what needs to be monitored to address the issue of interest, as is a full understanding of the physical processes and reactions taking place. For example, if with a set of metallurgical experiments based on compositional variation, an MLR expression of maximum significance is to be generated, knowledge of the main phases which form and their characteristics greatly assists the selection of which elements require monitoring and which elements do not.

A potential problem when selecting predictor variables is collinearity (highly correlated predictor variables). MLR estimates the effect of changing one variable while holding the remainder constant. When variables vary together it is almost impossible to separate the predictive effects of each variable alone. A result of collinearity is that the overall MLR expression is highly significant while individual variables show little statistical significance; by virtue of this it is impossible to detect which predictors are in fact related to the dependent variable. For example, in the current research, the results of an MLR analysis combining independent variables such as sample titanium content and cast grain size would be subject to the complications associated with collinearity. Collinearity may be assessed by correlating the independent variables against each other. However, this may be complicated by two predictors in combination predicting a third and so on. The best way to avoid collinearity problems is to intelligently select predictor variables at the outset.

Non-quantitative data can be included into MLR expressions by "dummy variables". These variables take values of either zero or one and can be applied to situations where any number of factors are needed. For example, if a machine operator producing tensile test bars reports that certain samples are very abrasive while all others are not, this factor can be included in regression analysis to predict downstream product properties or isolate the source of the abrasiveness. This would be achieved by assigning non-abrasive samples the dummy variable zero and abrasive samples one. If fatigue life was the parameter of interest, an expression as shown below may be generated:

$$\text{Fatigue Life (cycles)} = 160.4 \times \text{Tensile Strength (MPa)} - 0.513 \times \text{Porosity (\%)} + 10.31 \times \text{Ductility (\%)} - 5632 \times \text{Abrasive Rating.}$$

This expression indicates that whatever causes the abrasiveness is responsible for an average reduction in the fatigue life of 5632 cycles. While this in itself does not help solve or identify the problem, it quantifies the degree of one of its effects, allowing informed judgement as to what priority corrective actions should be given.

Generating an Appropriate Model

The simplest form of MLR model is a *first-order model.* This model contains each predictor without combination or transformation (as in the example above). First order models assume that the dependent variable changes at a constant rate relevant to the predictors over their entire range and that no interaction occurs among the predictors. *General linear models* use predictors which are non-linear or functions of combined recorded data. Examples of the former are squared, cubed and log terms while the latter may be the sum, product or a function of more than one of the recorded predictive variables. Clarifying this, if the expression for fatigue life given above contained the quality index Q (as mentioned in Chapter 2) as an independent variable, the model would be regarded as a *general linear model* not a *first-order model.* This is due to Q either containing a non-linear function or being a combination of more than one recorded variable (it is actually both).

Therefore

$$Y_i = 12 + 3A_i + 3.6B_i + 12C_i + E_i$$

and $$Y'_i = 12 + 3A'_i + 3.6B'_i\, C'^2_i + 12\log C'_i + E'_i$$

are both regarded as linear models in the MLR sense as the coefficients are all determined in a linear fashion. The first is a first-order model while the second is a general linear model.

A further form of independent variable manipulation which can be utilised are "lagged" predictors. Lagged predictors are used in time-series regression such as the prediction of monthly sales, etc. This form of variable is of little use in the context of the research outlined herein thus it will not be described in any detail. For the same reason, the issue of "autocorrelation" with regards to the time series will not be covered fully.

Contrary to common practice, running a simple first-order model does not constitute a full and competent MLR analysis. More competent MLR may be performed by following simple stepwise procedures such as forward selection and backward elimination. While these processes are simple, they are repetitive and become tiresome when large numbers of independent variables and combinations thereof are chosen as plausible predictors. Of the

several types of stepwise procedures, this research has employed the most common - *forward selection.* The alternatives which offer few real advantages will not be detailed, except to say that *backward elimination* is a similar, very common procedure. Non-stepwise approaches to model selection and development also exist, such as *Mallows*[175] *Cp statistic method,* however these procedures have not been pursued.

Forward selection involves running an MLR program with each predictor individually then selecting the one which produces the highest R^2 value. This first variable is then run in combination with each of the remaining variables and the set producing the highest R^2 is selected. The second variable found, need not have produced the second highest R^2 in the first variable selection pass. The third variable included by forward selection yields the highest R^2 value when combined with the first two and so on. The common method used to halt the process is to monitor the significance of the predictor values being added and the increment in R^2. To avoid stopping this process prematurely, the last added variable is usually limited to a statistical significance of over 80% to 90% (i.e. α = 0.2 and 0.1 respectively)* .

The exact form in which a variable should be entered into an MLR is often unclear. The problem of ascertaining the most appropriate form in which to enter a variable can often be resolved by plotting the variable in question against the analysis residuals. If this "residual" plot reveals any distinct trends, suitable manipulation of the variable can be used to improve the variable fit. For example, if the residuals display a maxima or minima, a squared variable function may be appropriate. This check for trends should ideally be carried out for each variable at each step in the regression process. Due to the continual reduction in variability associated with increased predictors, trends in the initial variables may not be evident until several subsequent factors have been added. Once a trend is detected and addressed the step process should be repeated using the new variable. This can sometimes mean starting all over again from the first step!

* α is a standard symbol for the uncertainty present in a statistically determined expression, for example 95% confidence implies α=0.05

Forward (or backward) selection should incorporate monitoring steps which allow re-testing of variables already included in (or excluded from) the model. During forward selection a variable included at one step as very significant may later be eliminated without an appreciable change in R^2. Full and proper MLR analysis with a large number of independent variables of unknown form and level of interaction is thus a complex and lengthy task!

A problem which arises from the use of stepwise regression is that biases are introduced and the R^2 value tends to become an overestimation. A result of this is that the coefficients also tend to be slightly higher than they should be, something which is not easily addressed.

Potential Problems

MLR analysis is subject to several potential problems such as skewness, outlier points, heteroscedasticity and pseudo-autocorrelation. Each of these problems, should they be severe enough and go undetected, has the ability to render an analysis worthless.

The most effective way to detect these problems is by close monitoring of the residual plots of each predictor variable. Computational factors exist to indicate each of these problems, however they are not infallible and are not incorporated into all program packages. Each of these problems is illustrated opposite in Figure 40.

Skewness due to a severely non-normal distribution of the MLR input data is usually only a problem with small sample sets. Certain packages include skewness factors, but they are not common. If serious skewness is detected in a residuals histogram the significance of the statistical prediction intervals (standard error) can become meaningless. Corrective measures to counter skewness include redefinition of the predictor form and alternate sampling methods.

Observations which clearly lie beyond the range of the remaining data, known as *outliers*, cause large distortions to the regression equations even when relatively large sample sizes are being analysed. Since MLR is based on minimising "squared" rather than "absolute" errors, numerous moderate errors are preferred to several small and one or two large ones.

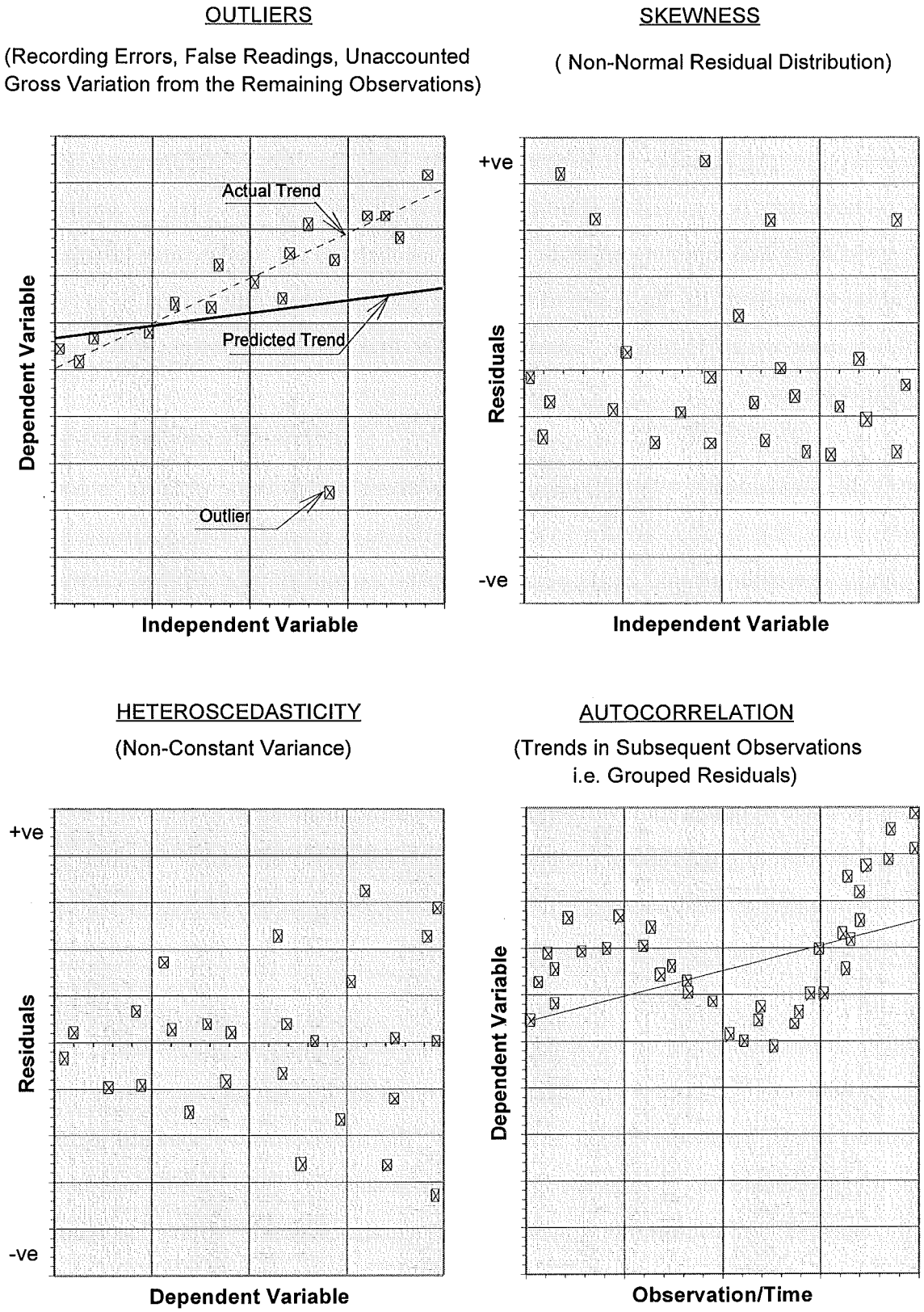


Figure 40: Common MLR problems.

By virtue of this, outliers can pose a serious problem. Looking at scatter plots and residual values, outliers can be difficult to detect as the MLR deliberately tries to minimise the magnitude of the deviation. One of the only failproof methods to detect outliers is to look for sudden changes in the output function while systematically eliminating each observation in turn from the MLR process. With large numbers of observations multiple observations may be omitted at one time. Thankfully, outliers can often be attributed to either recording and inputting errors or physical inconsistencies, so they may justifiably be corrected or omitted. In the event of not being able to justify elimination of an outlier, methods exist which minimise "absolute" rather than "squared" errors; this is termed "*robust regression*".

One of the fundamental assumptions of MLR analysis is that error variance is constant; unfortunately, this is often not the case. This problem is termed "*heteroscedasticity*" and no simple detection method exists other than visual examination of residual charts. The standard methods used to eliminate heteroscedasticity are redefinition of the dependent variable and a technique called "*weighted-least-squares*" which weights the influence of residuals depending on the magnitude of the associated independent variable. When physical recordings are made it is often difficult to maintain a constant error precision over the entire range of observation variability. A more difficult situation to deal with is when a large proportion of observations include one of two (or more) influential variables but not the two (or more) in combination. If this occurs it may be necessary to completely separate the data sets and analyse them separately.

Another assumption made by MLR analysis is that error terms are independent. In time-series, where data is collected at successive time intervals, it is not unusual for the residuals to display cyclic behaviour which is known as "*autocorrelation*". Standard techniques exist to detect this effect such as the Durbin-Watson statistic. These factors can, however, be the cause of confusion in non-time related situations. When a variable has a complex effect on the property of interest, as shown in Figure 41, it can be next to impossible to "fit" the trend with a matching function. When this occurs, residuals inevitably become semi-dependent and an autocorrelation detector will suggest a problem exists. The detector will have found a genuine problem, however it is not autocorrelation in the strict sense of

its meaning. Within this report this effect has been termed *pseudo-autocorrelation* as it is not related to the sampling method but is an indication that a perfect predictor function fit has proven elusive.

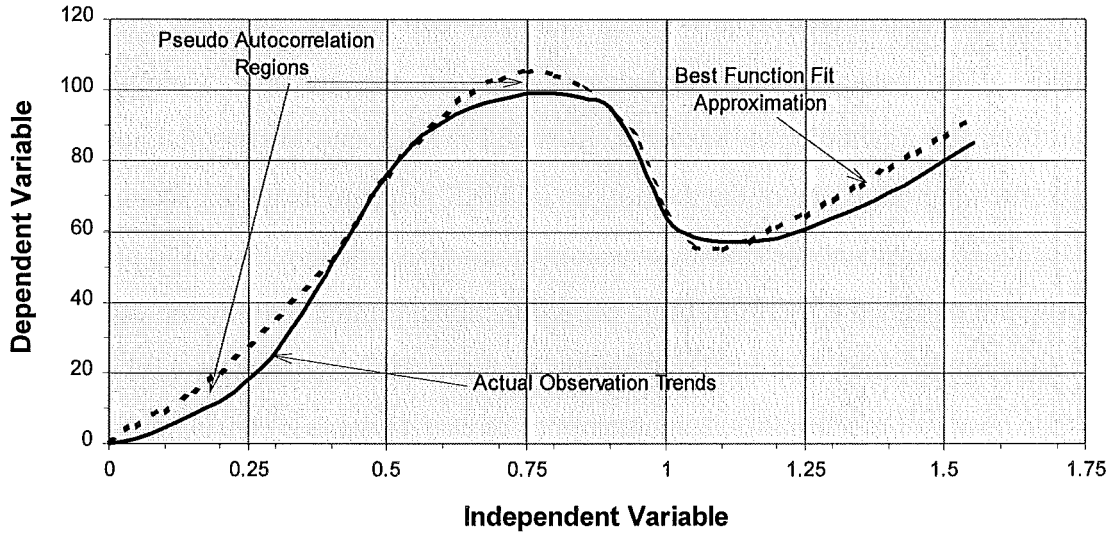


Figure 41: The creation of semi-dependent residuals by imprecise function fit (pseudo-autocorrelation).

The Use of MLR Results - Limitations

As already mentioned, MLR results must be used with due regard for the data from which they are generated. It must be remembered that while trends may correspond well between similar situations, quantified values may change drastically in magnitude. For example, modification will have similar effects but of varying magnitude in alloys subject to different cooling rates. Extrapolation is also complicated by MLR as the extrapolation error depends not only on the range of each predictor used to develop the regression equation but also on the correlations between the predictors. To avoid gross extrapolation errors, predictor values must be selected which lie within (or close to) the range of the observation values, not only variable by variable but also variable combinations. Hildebrand and Ott[176A] stress these points with the following comment: *"Those who try to forecast without regard to the data base on which the regression equation is built display a touching, childlike and possibly expensive faith in statistical magic"*!!!

7.1.3 Packages Available

Literally hundreds of computer packages are available which perform MLR analysis. All of these programs perform the same basic function by solving the regression equation, however several are limited in how much data they can process and how the output is presented. The packages investigated and used in the research were: Minitab, TexaSoft/Mission Technologies Kwikstat, IBM-SPFF-MLR and Microsoft Excel. These packages each represent one of the main types of MLR program available, namely: a well established, dedicated statistics package; a simple, relatively modern PC-based program; an older program designed to perform basic MLR functions, limited only by the capability of the machine upon which it is run, and finally, an up-to-date user-friendly package which utilises the power of modern PCs in an attempt to be easy to use and capable in the areas of data manipulation, statistics and graphical representation.

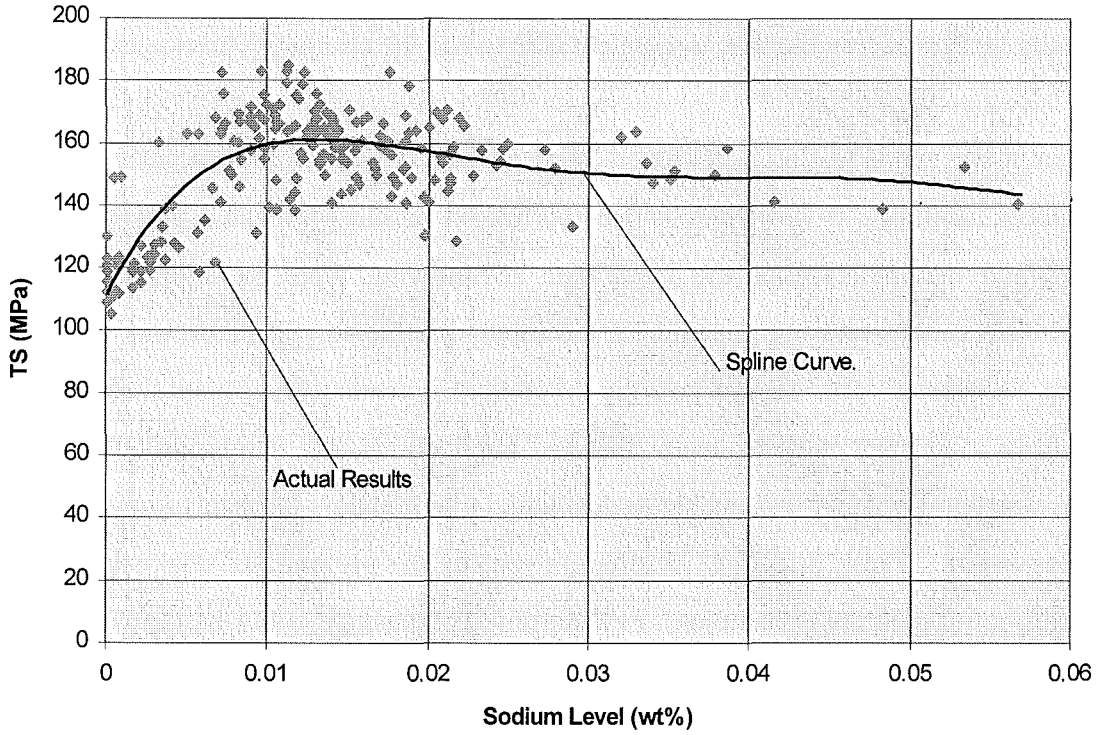
The first package evaluated was IBM-SPFF-MLR running on a Digital Micro-Vax computer. This program had been in use at the University of Canterbury for over 20 years and was showing its age, being particularly user-unfriendly! The main problems associated with the SPFF package were simply a function of the period in which it was developed. The data input and manipulation processes were exceedingly basic, as was the crude and minimalist output. The one feature the program had in its favour was an ability to rapidly process very large sets of data. Until recently, this feature has made it indispensable to researchers unable to gain access to dedicated statistics packages such as Minitab, SAS, etc.

Minitab is dedicated data analysis software which, from a statistics point of view, is more powerful than the other packages investigated. This program is very popular with statisticians and managers as it can easily be made to perform functions such as: weighted-least-squares to remove heteroscedasticity, monitoring for autocorrelation and isolating observations which are suspected outliers. Since the version of Minitab evaluated operated in a DOS environment, manipulation and graphical interpretation of input and output data was not particularly easy: this was found to be a major limitation. A further detrimental

point was that in the case of this research, the hardware required to run Minitab was physically far less accessible than equipment able to run the alternative packages.

An attempt was made to find a PC-based MLR package which would interface with a PC spreadsheet. Initially, it was thought that this would permit a repeated process of MLR analysis and manipulation of the input data so allowing rapid isolation/correction of suspect observations and optimisation of the input variable forms. This was carried out utilising "Kwikstat" and "Excel" as the MLR and spreadsheet packages respectively. Apart from a constant need to swap files and applications, the major limitation of this process was that Kwikstat was unable to deal with large numbers of observations (>400) or variables (>10). These packages were employed for the preliminary analysis of results from non-boron containing samples. Few definite conclusions could be drawn from this work which was presented at the 1994 IPENZ Conference; the associated paper is contained in Appendix Q - IPENZ - '94b.

Subsequent to the analysis mentioned above, updated PC facilities (486-66 with 16Mbytes RAM) enabled the MLR routine within Microsoft Excel to efficaciously process the full set of 495 observations with as many predictors as desired. The real advantage of this development was the ability to rapidly order, manipulate and graphically interpret MLR input and output data without having to change applications. Whilst Excel is not at present capable of the more advanced functions available within packages such as Minitab, it has inherent advantages which, in this case, outweigh any deficiencies. As a result of this, Excel was used to perform all of the remaining MLR analysis in this research. Excel deposits all statistical data output, residual graphs and residual lists directly onto spreadsheets so they may be later manipulated and analysed using standard spreadsheet functions. For example, all residuals and residual plots may be viewed at once so any suspected outliers can be adjusted and the effect of this change relative to each predictor simultaneously monitored. Another function which is not available on the other packages tried, is an ability to "fit" curves to plotted data. An example of the use of this feature was that the complex modification residual trends due to strontium and sodium addition could be "fitted" with best-fit functions. These functions could then be added directly into the regression as sodium or strontium predictors (See Figure 42). The application of this



Spline displayed above as fitted by Microsoft Excel.

$$y = 1{,}607{,}274{,}667.48x^5 - 310{,}033{,}682.03x^4 + 22{,}289{,}787.70x^3 - 730{,}313.43x^2 + 10{,}231.75x + 110.99$$

$$R^2 = 0.61$$

Figure 42: Generation of the sodium vs TS spline.

technique within an MLR process is indicated by predictors which are listed as "splines". Particular caution must be applied when using models employing splines as these functions only follow the test data within the test data range. Inputting data into these expressions which deviates even slightly from the initial test range is liable to produce spurious results. Care must also be taken to use the full numerical spline expressions provided as minor truncation will result in substantially different function characteristics.

7.2 INTERPRETATION AND EXPRESSION OF MLR RESULTS

7.2.1 Numeric Output

Almost all computer packages which perform MLR analysis output results in a similar fashion. The output of a Microsoft Excel MLR as used during this research is shown in Figure 43. This output is somewhat clearer and more user-friendly than most package outputs. The example illustrated is a regression output relating the composition of strontium modified samples to Vickers hardness.

The main output features and their significance are listed below:

A. The Coefficient of Determination (R^2)

This factor is a direct indication of the proportion of the variation in dependent variable that is explained by the MLR model. In this case the regression model explains 85-86% of the variation in the measured hardness readings.

B. Standard Model Error (S_E)

The standard error or standard deviation associated with predictions using the current model is 1.51 Vickers Hardness units (kg/mm^2).

C. The Number of Observations Used

This model was constructed by regressing 294 sets of data, e.g. 294 sample results.

D. Fisher (F) Statistic

This statistic indicates the worth of the overall model in statistical terms. The higher the F-statistic the more statistical weight is given to the model. Standard F-distribution tables exist to convert this value to a level of significance dependent upon the number of predictors used and the number of observations in the input data.

SUMMARY OUTPUT			Hv10 Sr Samples			
Regression Statistics						
Multiple R	0.925374					
R Square	0.856316					
Adjusted R Square	0.851763					
Standard Error	1.509993					
Observations	294.					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	9	3859.184285	428.7982539	188.062781	4.065E-114	
Residual	284	647.5428238	2.280080366			
Total	293	4506.727109				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	22.168905	2.008463096	11.03774584	8.2942E-24	18.21554449	26.12226586
Magnesium	42.192466	2.00903462	21.00136349	9.5543E-60	38.23798066	46.14695195
n^2 Si Spline	-0.094789	0.00773802	-12.24979656	5.5234E-28	-0.110020305	-0.07955803
Iron	7.097372	0.585525295	12.12137547	1.5539E-27	5.94485255	8.249891351
Titanium	10.408894	1.356014545	7.676092827	2.6529E-13	7.739780706	13.07800634
Manganese	6.544656	0.898099241	7.287229747	3.1421E-12	4.776880812	8.312430197
n^2 Sr Spline	847.384380	157.4541918	5.381783555	1.5453E-07	537.4592374	1157.309523
$(Fe+0.05)*Mn^2$	-13.193626	3.08283065	-4.279711434	2.5613E-05	-19.2617189	-7.12553226
Ti B	-83.202621	15.96407712	-5.211865416	3.6022E-07	-114.6255313	-51.7797115
AREA	-0.652013	0.304760467	-2.139429041	0.03325336	-1.251889018	-0.05213777
Sr Spline	$=Sr^2-0.093*Sr$					
Si Spline	$=Si^2-34.3*Si$					

UNUSUAL OBSERVATIONS		
Observation	*Predicted Hv10*	*Residuals*
67	50.67444444	-3.456777777
211	43.83333333	4.888888888

D -W Stat	1.97

RESIDUAL OUTPUT			
Observation	*Predicted Hv10*	*Residuals*	*Standard Residuals*
1	45.30372146	-2.503721456	-1.658100819
2	45.11193402	-4.11193402	-2.723146837
3	48.389864	-0.489863999	-0.324414641
4	48.88625038	-1.186250382	-0.785599662
5	47.27018304	-2.570183037	-1.7021153
6	47.37512322	-2.075123222	-1.374259706
7	47.58856821	-1.688568214	-1.11826191
8	46.96752115	-1.767521153	-1.17054885
9	48.45287698	1.147123023	0.759687392
10	45.22688478	-2.526884785	-1.673440837
		⋮	
		⋮	
290	56.97654809	2.723451913	1.803618304
291	54.42801123	-1.028011235	-0.680805074
292	56.42732902	-1.127329025	-0.746578727
293	54.72516647	-0.325166466	-0.215342957
294	55.78710093	0.812899074	0.538346075

Figure 43: The layout of Microsoft Excel MLR output.

E. Significance of F

Sometimes called a p-statistic, this value is a measure of the significance of the MLR expression as a whole and how it performs in relation to a simple mean value estimation. Very low significance (# >0.05) indicates that none of the independent variables contain appreciable predictive worth. In this example the probability of the overall MLR equation being a less advantageous predictor than the mean hardness is 4.1×10^{-114}% - i.e. nil.

It is possible to have a model which has a very low R^2 value yet an F statistic which is very significant. In such a case the MLR model can explain only a small proportion of the dependent variable variation, yet statistically the equation is worthwhile and the predictors used definitely have predictive worth. This situation is a good indication that only some of the influential factors affecting the dependent variable have been included in the model - more significant independent variables need to be found.

F. Coefficients

These values are the calculated coefficients of the linear equation. The units these factors have is totally dependent on the form in which independent and dependent variables are entered. In this case they are kg/mm^2 per wt%. The equation indicated by the above output is:

$$\begin{aligned} H_{V_{10}} = {} & 22.1689 + 42.1925.Mg\% - 0.0948.(Si\%^2 - 34.3Si\%) + 7.0974.Fe\% \\ & + 10.4089.Ti\% + 6.5447.Mn\% + 847.3844.(Sr\%^2 - 0.093Sr\%) \\ & - 13.1936.(Fe\% + 0.05).Mn\%^2 - 83.2026.Ti\%.B\% - 0.6520.Area^* . \end{aligned}$$

The coefficients are a direct indication of the influence the various predictors have, for example an increase of 0.2% iron can be expected to cause hardness to increase by $0.2\times7.0974 \cong 1.4$ kg/mm^2. Care must be taken in the interpretation of the "intercept" value as the intercept corresponds to all of the predictors having zero values. In this case, this amounts to a huge extrapolation as all samples contained at least 9.5% Si and 0.1% Fe. (This extrapolation is worsened by the silicon term being a quadratic spline.)

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* Area refers to porosity area as described in Section 6.2

G. Standard Coefficient Error

This is the standard deviation associated with the individual coefficients.

H. *t*-Statistic

This statistic is analogous to the F-statistic. It indicates the predictive worth of the independent variable in question. The higher the modulus of t ($|t|$) becomes the more significant the predictive worth of the individual variable.

J. P-Value (Coefficients)

The P-value for the coefficients is similar to the F-significance value (or P-value model) in that it provides a measure of the level of significance which can be associated with the respective predictors. In this case, the probability of the magnesium coefficient being zero (in other words, magnesium having no predictive worth) is 9.55×10^{-60}%. If the P-value of any MLR term is ≥20% it should be excluded from the model.

K. Upper and Lower 95%

These values are simply an indication of the plausible range that the various predictor coefficients may have. In the given example, the probability of the magnesium influence being zero is nil and with 95% confidence, the magnitude of influence is between 38.2 and 46.1 kg/mm^2 per wt% magnesium present.

L. Unusual Observations

Certain packages (Excel is not one) automatically list observations which have unusually high residuals in comparison to the mean residual. This can be helpful in establishing outliers but it is not infallible for the reasons mentioned above under "Potential Problems".

M. Durban-Watson Statistic (DW)

Some dedicated statistics packages calculate this statistic. It is an indication of possible autocorrelation. Ideally, the DW statistic should equal 2.0; if values less than $\approx$1.6 are observed autocorrelation can be suspected.

N. Output of Individual Residuals

These lists are indispensable as they allow identification of outliers and when observations are entered in an intelligent manner they can assist in the identification of influential factors and predictor interactions which may otherwise go unnoticed. An example of the latter is that, in the course of this research, it was expected that iron and manganese would interact due to the formation of $(FeMn)_3Si_2Al_{15}$. Several predictors combining these elements were tried in the Vickers hardness forward-selection process, however none proved to be capable of improving the overall model by a significant margin. In an attempt to elucidate the presence of a complex interaction, the samples were arranged into high (>0.3%) and low (<0.3%) iron levels and then into subsets of ascending manganese level. When a residual plot was constructed from the observations in this order, significant pseudo-autocorrelation could be seen. The pseudo-autocorrelation was a clear indication that a Fe/Mn interaction was taking place. This led to the work outlined in Section 8.2. It could be expected that plotting a three-dimensional residual chart of the suspected related predictors and the dependent variable would highlight residual trends and so assist in the derivation of suitable interaction functions. No conventional statistics packages incorporate this feature although manipulation of the output data within spreadsheets such as Excel makes this idea feasible. This course of action was carried out several times during the reported research whereupon it became obvious that interpreting such plots which incorporate appreciable unexplained scatter is exceedingly difficult. The only method to fully utilise such 3D plots would be to enter them into an advanced mathematical package capable of smoothing and surface-fitting in three dimensions.

7.2.2 Graphical Results

Residual Plots

All MLR programs produce charts of the residual values versus the various predictor variables. As mentioned above, these charts are important during model development, but have little value as a representation of MLR results.

Dependent vs Predicted (Observations vs Predicted Results)

A standard technique for displaying the effectiveness of an MLR analysis is to plot the dependent variable versus the predicted values. Ideally this should generate a line of points running diagonally across the chart as shown in Figure 44. As all observations resulting from experimentation have some degree of associated uncertainty the best results that can be expected from a ideal MLR will be contained within a scatter bounded by the experimental error range.

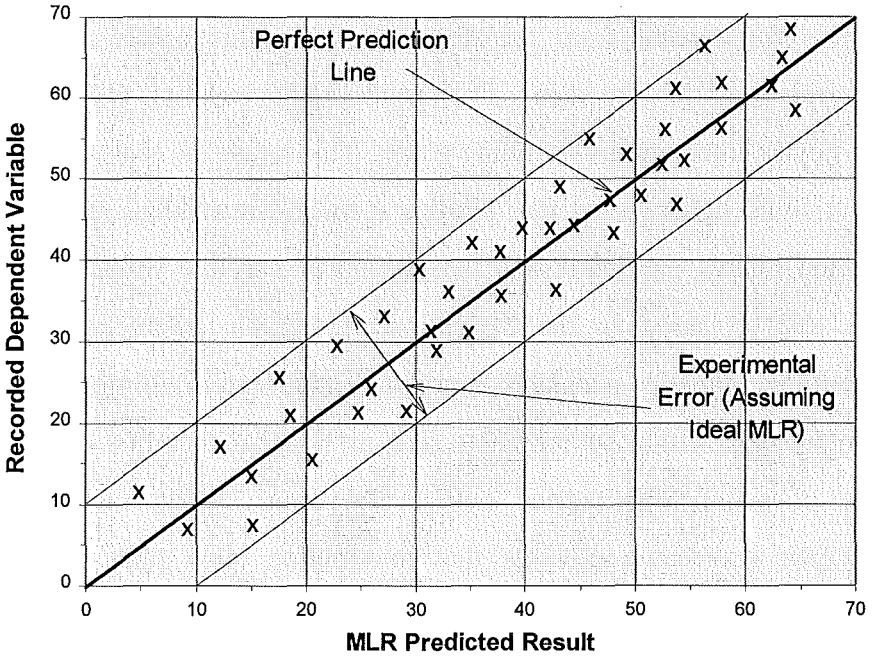

Figure 44: An idealised observation vs predicted plot.

Function Plots, 2D & 3D

One of the most effective means of displaying MLR output is by plotting the predictor functions versus the appropriate dependent variable. When a model can be displayed on a single chart or when the non-displayed predictors are predominantly zero, absolute values (i.e. incorporating the intercept term) can sensibly be used on the dependent axis. This allows predictions to be read directly from the chart. If a model consists of more than two independent variables and an interaction function then multiple charts must be used. When this is the case, the dependent axis is displayed as variation from a specified datum. This allows easy assessment of the cumulative effects of the various predictors. Since predictor functions are generated outside of, and prior to, the MLR process, prediction charts cannot be generated automatically.

8.0 STATISTICAL ANALYSIS RESULTS

8.1 CONTAMINATION DURING ALLOY AND IMPURITY ADDITIONS

8.1.1 Monitored Elements

The OES composition data for all of the cast specimens (Appendix H) was analysed to reveal the extent to which deliberate alloy and impurity additions had inadvertently varied other element levels. Of the 21 elements analysed, variations in several (Zn, Sn, Li, Be and Bi) were obviously insignificant while others (Cu, Ni, Pb, Cr, Ca, V, Ga and Zr) were subjected to correlation analysis (ANOVA) and regression against the controlled variable elements (Si, Fe, Mn, Mg, Ti, B, Na and Sr). Correlations in variance among the control elements were also assessed. The potentially significant contamination factors which could not be assessed by ANOVA and regression analysis included introduction of elements other than those monitored by OES (notably phosphorus) and the introduction of inclusions or coarse particulate.

The above analysis revealed no significant effects or correlations relating to the levels of Ni, Pb, Cr, Ca, V, Ga and Zr, and hence these elements were largely omitted from any further MLR analysis. On some occasions some of these seemingly insignificant elements were included in preliminary MLR analysis, but in no instance were these elements revealed as statistically worthwhile predictors. The only element outside the control group which displayed variations at a potentially significant level was copper. Expectations were that samples to which deliberate CuP additions had been made would display significant increments in copper level. This proved not to be the case, as variations in these samples were indistinguishable from those in the remaining melts. The two samples displaying the most pronounced copper levels were "extras" produced from prior melt scrap. It is thought that this scrap must have been inadvertently mixed with small volumes of copper-containing alloy. Surprisingly, ANOVA failed to correlate the copper levels of the remaining samples with any of the melt additions made. Since copper variation was significant the level of this element was included in all MLR analysis. The strong

influence that the high copper samples had on the regression weighting was closely monitored in all MLR results.

Of the control element variables, only iron displayed variations which could be associated with the addition of other elements. Boron additions, whether from the 3%B or the 5%Ti:1%B alloy, resulted in detectable increases in iron. Since these increased iron levels were subject to some variability and were typically below 0.04%, no quantified contamination factors could be accurately established. The iron level of the 3%B master alloy as stipulated by the supplier (0.12%) was below that of the base alloy (0.19%) so this contamination was unexpected. (The iron level of the 5%Ti:1%B alloy was unknown.) It is possible that the recorded increases in iron level could have been caused by correlation errors within the OES analysis equipment. This possibility was largely discounted as microstructures of the boron-containing alloys displayed noticeably more of what was assumed to be iron phase than the stipulated iron content would suggest. Large additions of the strontium master alloy were also noted as causing slight increases in iron level. Once again this effect could not be accurately quantified.

8.1.2 Deliberate Phosphorus Addition

The effects of phosphorus described in Section 2.7 suggest that the ten samples cast with deliberate phosphorus additions (see Sections 3.2 and 3.3) should not have displayed property results consistent with the remaining specimens. The property degraded most by phosphorus is modification and accordingly, the effects on this property in the ten treated samples was closely monitored. The first, full, MLR analysis conducted was for modification and initially all 495 specimen results were separated and analysed in sets of either sodium or strontium modified samples. The boosted phosphorus samples in these sets were then isolated and their fluctuation from the MLR prediction results assessed. If phosphorus additions were significant then the recorded modification levels should have been substantially lower than the MLR generated predictions. Figure 45 displays the ten phosphorus-boosted sample results from the two regression sets; clearly these results are the opposite of what was expected. The results show that seven of the ten samples displayed higher modification ratings than predicted and no results varied from the MLR results by an unusual amount. The only conclusions that could be drawn from this result

were that either minimal phosphorus was recovered from the CuP additions or the phosphorus failed to act in the anticipated way. The former possibility is supported by the negligible increases in the copper level recorded for these samples.

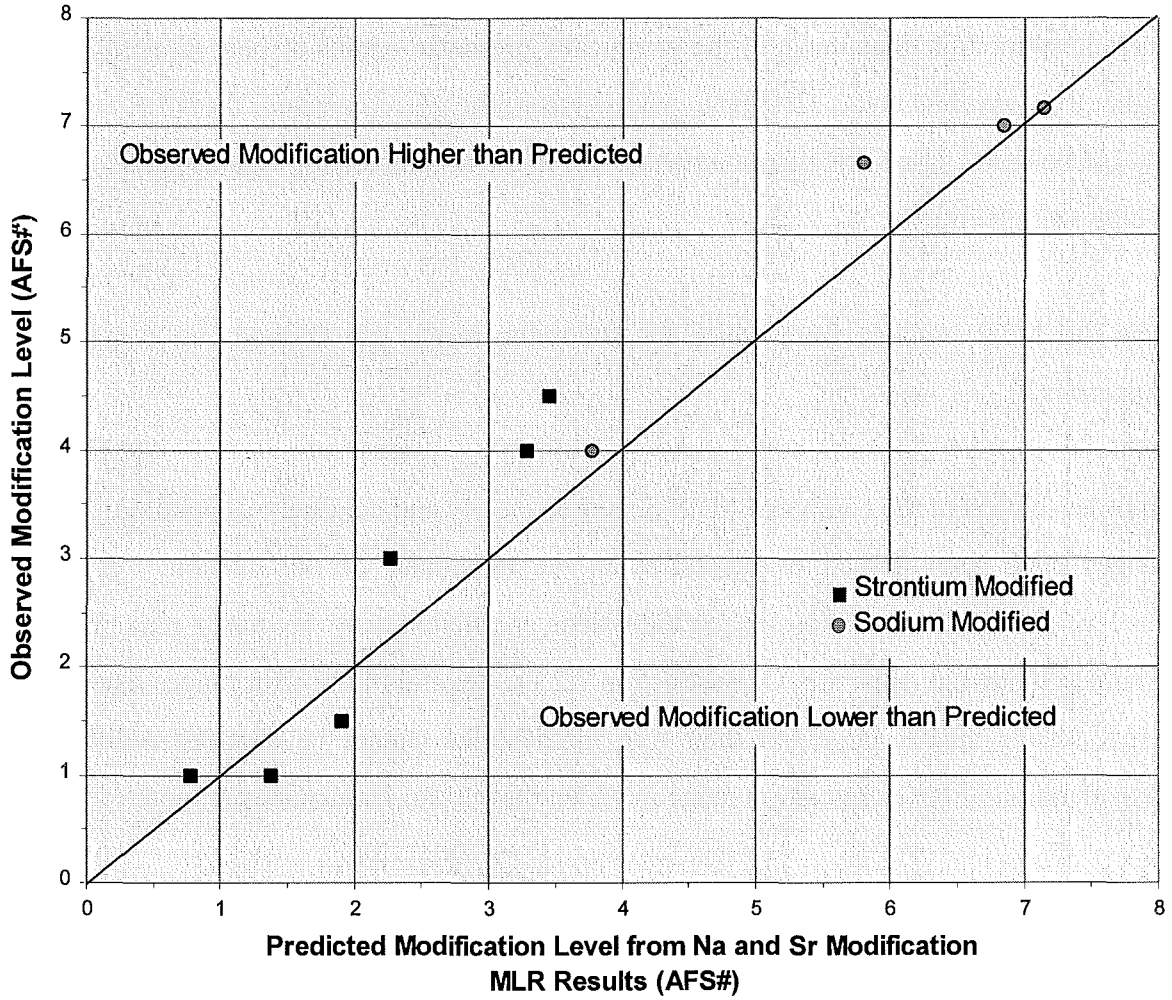

Figure 45: The modification variation of samples subject to phosphorus addition.

By virtue of the above findings, the boosted phosphorus samples were not excluded from the MLR modification observation set. Irrespective of the properties being investigated, MLR analysis found no atypical behaviour which could be associated with the phosphorus boosted samples. These samples have thus been regarded as valid observations in all of the results presented in the following sections.

8.2 RELATIONSHIPS BY PHYSICAL PROPERTY

Since almost all of the MLR results presented in the following sections are complex and include spline functions, most of the graphically presented results display property *change* rather than *absolute* value. To obtain predictions of the *absolute* values the MLR equations should be used. The MLR output terms shown in the accompanying figures are denoted by a club (♣) superscript.

The full MLR outputs, from which the following results are derived, are contained in Appendix O.

In order to present the computed MLR results as clearly and concisely as possible, no error ranges have been quoted or illustrated in the remainder of this section. The error associated with each expression or individual coefficient may be easily read from the results provided in Appendix O (see Section 7.2.1). Several of the error ranges listed in the MLR results appear large but their true implications cannot be assessed without due consideration of the composition range in which the various elements were monitored.

8.2.1 Modification Level

The MLR results given below relate the sample composition (wt%) to the AFS modification rating, as defined in Section 6.1. The 495 samples monitored have been separated into two groups and regressed depending upon the major modifier used. Copper has been excluded from the regression equations even though it was found to be a highly significant variable in each set (p-value << 0.2). This was done as the removal of copper from each set of all significant variables resulted in virtually no loss in the predictive worth of the final MLR equation (R^2). The exclusion of copper increased the significance of both the iron and titanium terms yet no direct correlation between these elements could be found. It should be noted that the copper terms which were established were incompatible and difficult to explain. A regression of the full set of data was carried out in the hope of establishing the interaction between sodium and strontium - the results of this work are presented separately.

Overall Modification Equations

Sodium Samples

$$\text{AFS Modification \#} = 83{,}833{,}388.(\text{Na Spline})^{*} - 152{,}876{,}158.\text{Mg}.(\text{Na Spline})^{*} + 2{\cdot}8315.\text{Ti}^{*} + 0{\cdot}965262.\text{Fe}^{*} + 0{\cdot}348226$$

$$R^2 = 0{\cdot}906$$

$$\text{Na Spline} = \text{Na}^5 - 0{\cdot}17306.\text{Na}^4 + 0{\cdot}011192.\text{Na}^3 - 0{\cdot}0003593.\text{Na}^2 + 7{\cdot}0776\text{E} - 6.\text{Na}$$

Strontium Modified Samples

$$\text{AFS Modification \#} = -731{,}626{\cdot}59.(\text{Sr Spline})^{*} + 1{,}883{,}8122.\text{Mg}.(\text{Sr Spline})^{*} - 0{\cdot}27922.\text{Si}.\text{B}^{0.3*} + 3{\cdot}8796.\text{Ti} + 160{\cdot}983.\text{Na}^{*} - 0{\cdot}040417.\text{Fe}^{*} + 1{\cdot}227111$$

$$R^2 = 0{\cdot}7044$$

$$\text{Sr Spline} = \text{Sr}^4 - 0{\cdot}20533.\text{Sr}^3 + 0{\cdot}01432.\text{Sr}^2 - 0{\cdot}0004062.\text{Sr}$$

As can be seen a Si-B term was found for the strontium samples, yet no statistically significant similar term could be found for the sodium samples.

The independent variables given in the above (and all subsequent) expressions are listed in order of statistical significance (two tailed t-test). The sodium spline term in the sodium expression is significant to the $1.1 \times 10^{-90}\%$ level while the iron term is significant to the 0.001% level. The latter significance implies that there is a 1 in 100,000 chance that the iron term is of no benefit to the above sodium sample equation. The similar terms in the strontium equation are $2.3 \times 10^{-54}\%$ and 4% respectively.

It should be noted that the AFS modification number of six represents a very fine "super modification" state. As very few samples displayed regions with this degree of refinement, the MLR predictive rating of six can be assumed to be made up of a very well-modified structure with some regions of over-modification. Optimal refinement can be assumed to be predicted with a rating of 5.5.

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* This term should be eliminated if the full modifier-interaction terms given later in this section are used.

Sodium (and Magnesium)

The 3D diagram shown in Figure 46 illustrates the modifying effects of sodium and the interaction magnesium has upon this eutectic refinement. Optimal modification in the absence of magnesium occurs at around 0.015%Na which is in close agreement with the sodium requirement for optimal physical properties, as mentioned in Sections 8.2.5 - 8.2.7 below. When magnesium is added, it is predicted that maintaining a similar level of eutectic refinement requires increased sodium levels. For optimal modification the predicted sodium requirement rises by as much as 66%, for example, 0.025%Na is required when the magnesium level reaches 0.12%. Further investigation of this issue would be interesting as the additional modifier in the presence of magnesium does not appear to translate into improvements in strength. As possible explanation for the above findings is discussed in Section 9.3.

Strontium (and Magnesium)

When interpreting Figure 47, which shows the modification effects of strontium and magnesium, it should be noted that the strontium model has a higher base (or intercept) modification level than the similar sodium model. The variation in the base values can be partially explained by the variation in iron terms and possible heteroscedasticity around the zero axis of the strontium data.

As shown later in Figure 75, optimal physical properties have been found to occur with 0.028 - 0.035%Sr. This corresponds to a modification rating of approximately 4. Strontium was not as effective at eutectic refinement as sodium; it also caused far less uniformity in the eutectic structure. Consequently, over-modification was not as pronounced and ratings beyond 4 almost certainly indicated very excessive levels of modifier. As illustrated, optimal modification appears to be available over the range 0.02 - 0.05%Sr. Unfortunately, this wide composition range for optimal micrographic rating does not correspond to a wide composition range for optimal physical properties (see following sections). A consequence of the above point is that accurately detecting the optimal physical state via microscopy is difficult, if not impossible.

Magnesium displayed similar properties in the strontium samples as it did in the sodium set; it coarsens the structure by hindering the action of the modifying element. For a given level of modifier addition, the action of magnesium was similar, meaning that the

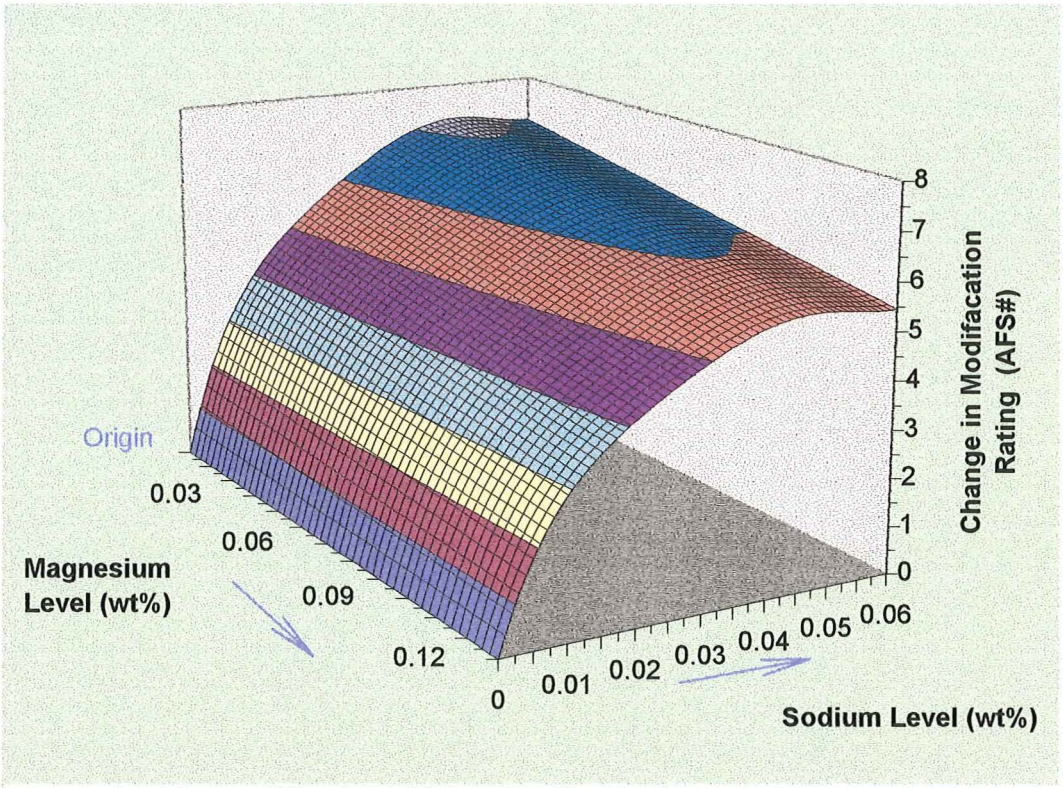


Figure 46: The modification effects of sodium and magnesium on sand-cast Al-Si eutectic alloy.

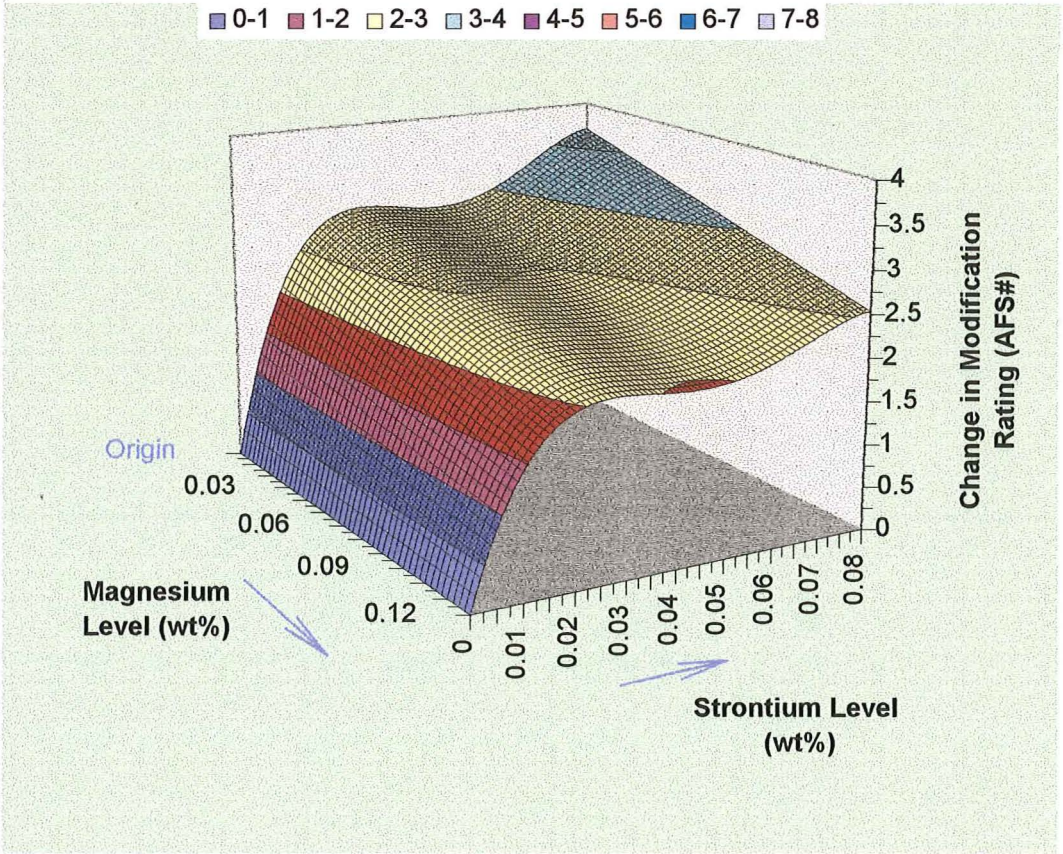


Figure 47: The modification effects of strontium and magnesium on sand-cast Al-Si eutectic alloy.

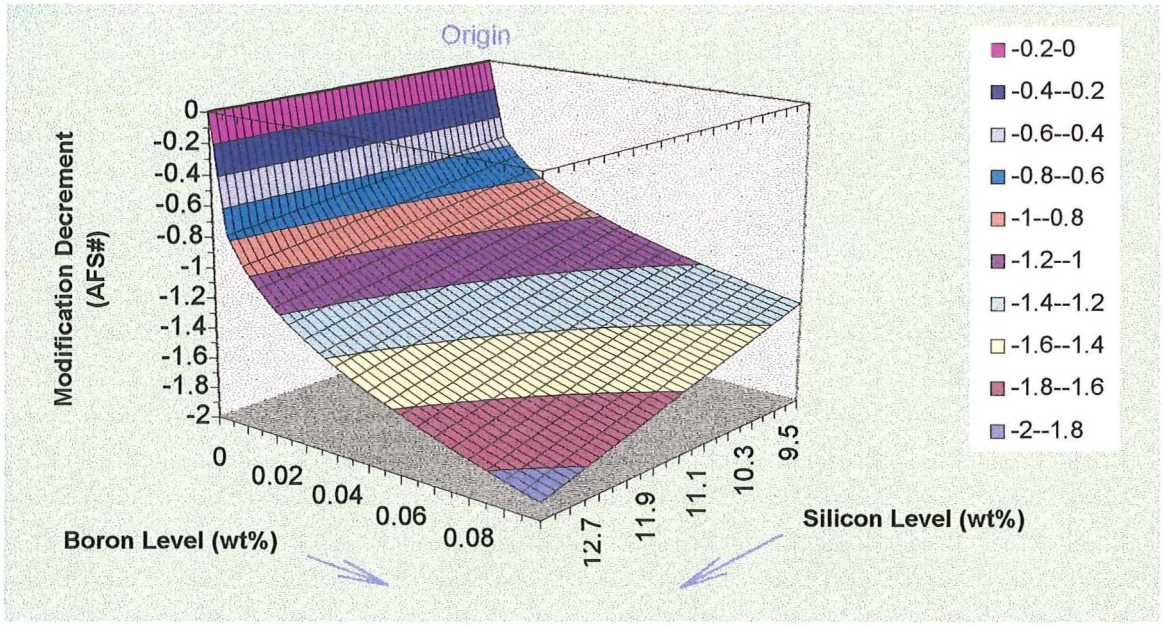


Figure 48: The modification effects of silicon and boron on sand-cast Al-Si eutectic alloy.

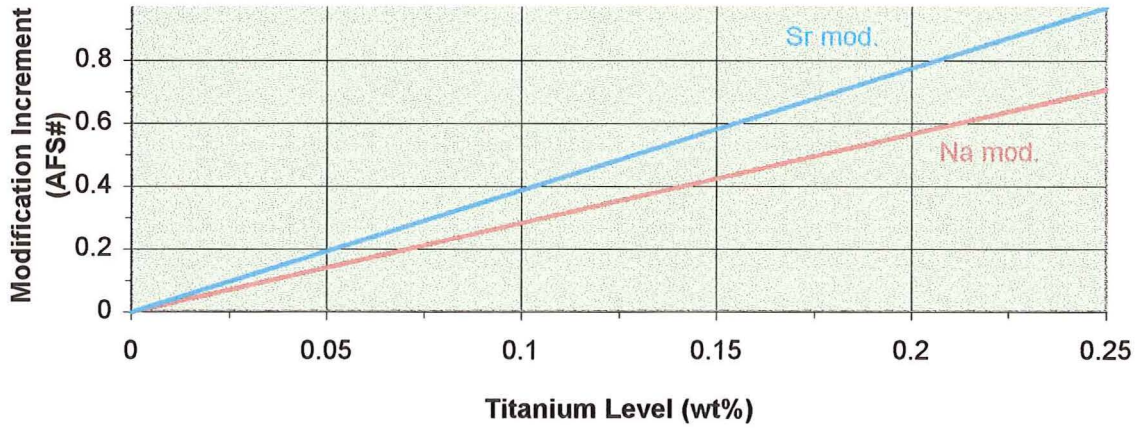


Figure 49: The modification effects of titanium on sand-cast Al-Si eutectic alloy.

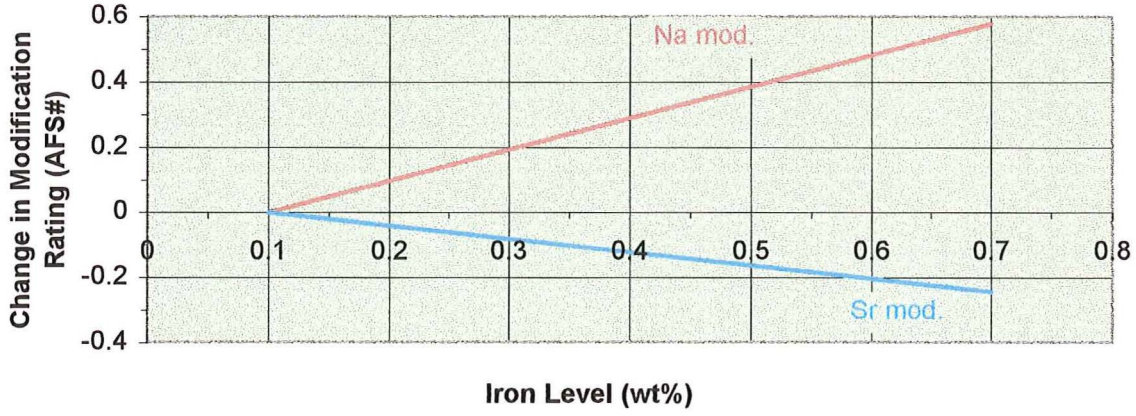


Figure 50: The modification effects of iron on sand-cast Al-Si eutectic alloy.

magnesium effect was more pronounced in the less modified strontium samples than those containing sodium. At equivalent modification ratings, the coarsening effect of magnesium was approximately 44% stronger with strontium than sodium.

Silicon and Boron

The strontium regression expression contains a highly significant term relating the boron and silicon levels to modification; a similar term was not found for the sodium set. Even though considerably fewer samples containing boron were sodium rather than strontium modified, the lack of a Si-B term in the sodium set is not easily explained. Numerous Si-B predictor possibilities were tried in an attempt to include such a term in the sodium sample results, however none proved significant.

Figure 48 shows that the addition of boron is highly detrimental to strontium modification, a situation which gets worse as the silicon level increases. It is apparent that even very minor boron levels have significant detrimental effects on the modification level achieved. This is in agreement with the boron ductility function, which appears in Section 8.2.5.

Titanium

Titanium has proven to be beneficial to silicon refinement. Since expressions incorporating possible interactions between titanium, boron and the conventional modifiers proved worthless in the explanation of silicon refinement, titanium must act via a mechanism independent of these elements. Sigworth[13] states that "*successful modifying elements must be able to combine with phosphorus but not aluminium*". Titanium does not meet either of these requirements. Sigworth also goes on to mention a publication* which indicates that titanium has no effect on modification of Al-7%Si-Mg alloy. This observation may be partially explained by the fact that in the indicated research, titanium was added in conjunction with boron. The results illustrated in Figure 49 clearly show that titanium *does* refine eutectic silicon. Of the two titanium terms the one with the lower statistical significance is still significant to the 1.5×10^{-6}% level, i.e. this trend is indisputable. As illustrated, the results indicate that titanium is a more powerful refiner in the coarser strontium structure than the finer sodium equivalent.

* Sight-unseen - Gobrecht J., "The Influence of Alloying Elements on the Duration of Modification of Na and Sr in Al-Si Cast Alloys", Giesserei, Vol 65 (1978), pp158-164.

Several functions incorporating boron were included in the MLR process with the aim of establishing whether titanium acts independently or if the modifying action stems from removing the detrimental effects of boron by formation of titanium borides. Since no Ti-B function could be established, the indication was that titanium acts directly on the eutectic silicon rather than promoting some secondary modification effect.

Iron

Iron displayed a statistically significant (0.001%) beneficial modification effect on the sodium modified samples. This was not in agreement with the strontium results as they implied that iron is detrimental. While the strontium-iron term is only significant to the 4% level, this is high enough to establish that iron is indeed detrimental. This leads to the conclusion that iron acts in opposing ways depending on the type of modifier employed (See Figure 50).

Manganese

Manganese levels did not show any influence on modification.

Modifier Interactions

When it was not practical to clean the crucible or foundry tools between melts using different modifiers, minor carry-over contamination occurred; in addition, the "extra" scrap remelt samples inevitably contained both modifying elements. While cross-contamination was very minor, the effect it had on modification levels was able to be assessed. By carrying out an MLR analysis on the combined sodium and strontium samples it was possible to establish a statistically significant (5×10^{-4}%) interaction term. The full output of this MLR is included in Appendix O Section One, but the only data it contains of true relevance are the sodium and strontium spline terms and the interaction term itself. As with any MLR-derived expression based on splines, the interaction term is only relevant within the bounds of the input data. In this case the interaction term is limited to the ranges 0 - 0.003%Na with 0 - 0.04%Sr and 0 - 0.0025%Sr with 0 - 0.024%Na. These regions cover all of the modifier combinations included within the observation data.

Since the MLR output includes the modifier effects as splines and an interaction term, all of these factors must be combined when assessing the overall interaction effects. For

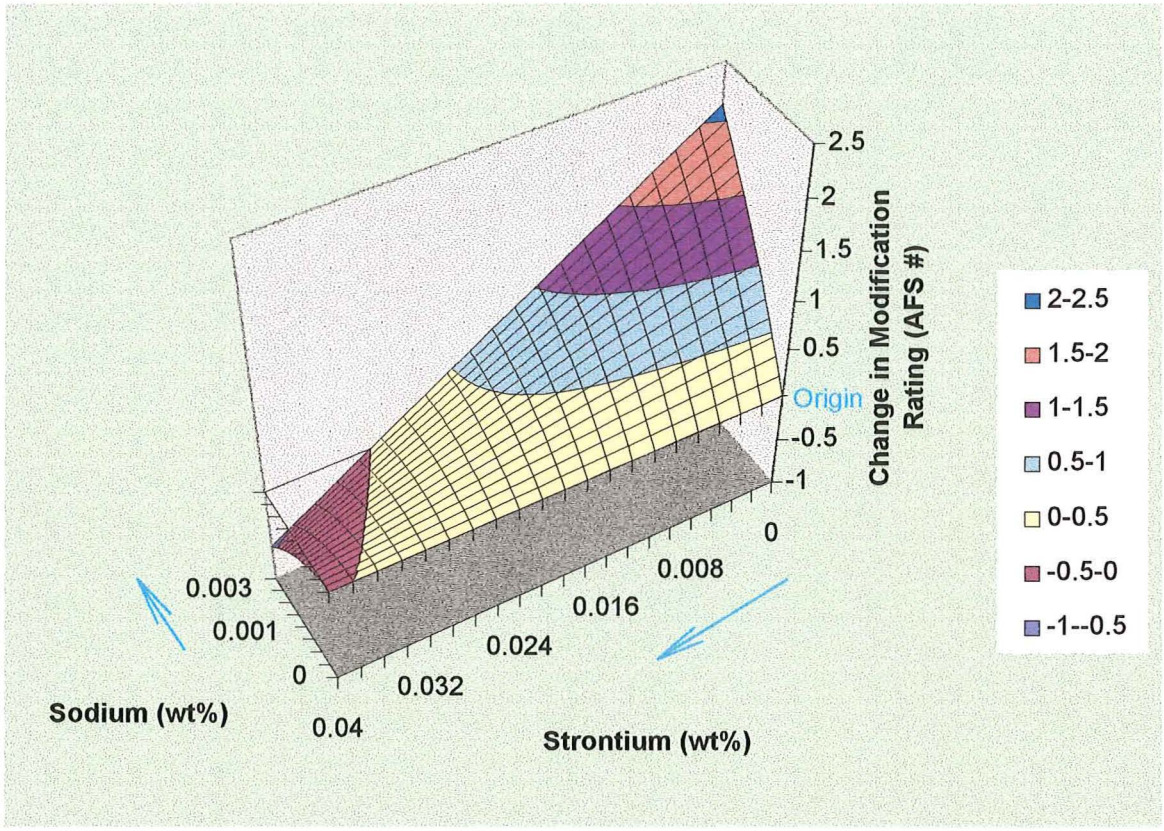


Figure 51: The effect of sodium in predominantly strontium modified samples.

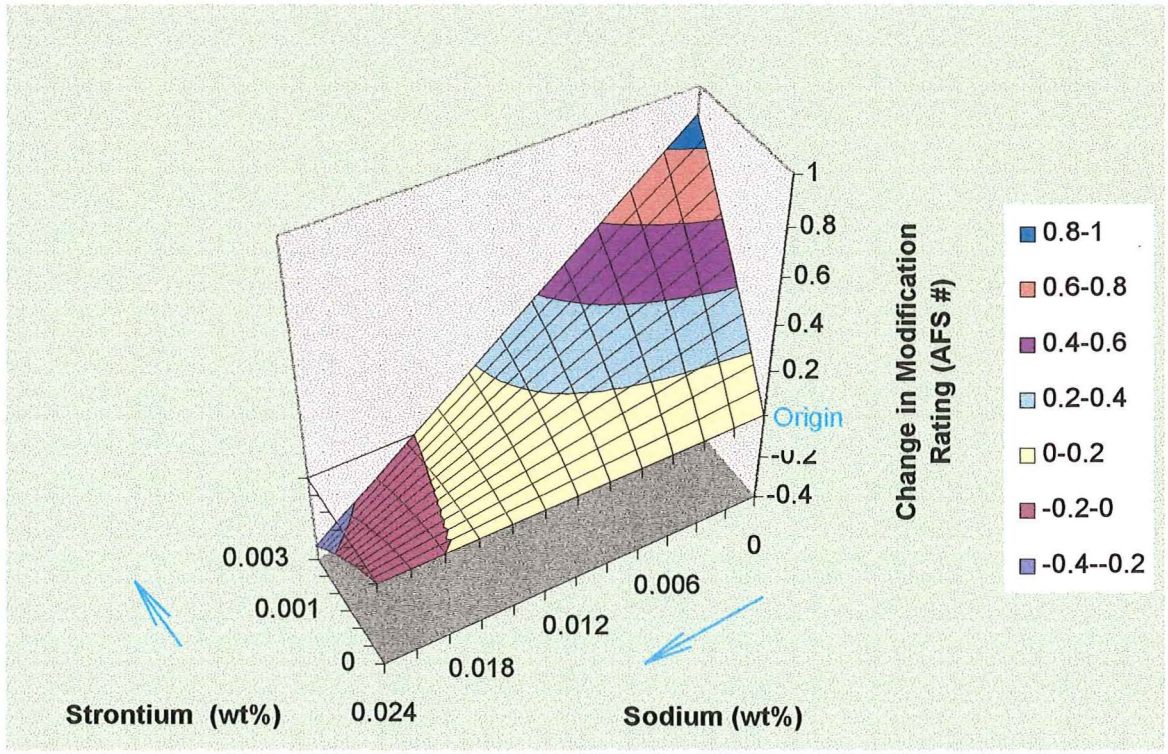


Figure 52: The effect of strontium in predominantly sodium modified samples.

example, although the interaction term is negative in combination with the splines, the overall effect may be positive or negative. The following functions exclude the dominant modifier term so that only the secondary modifier effect is established. This allows the expression outputs to be combined directly with the relevant sodium and strontium expressions given above.

Sodium Effect in Predominantly Strontium Modified Samples *(see Figure 51)*

$$\text{AFS Modification \# Increment} = 90{,}681{,}062.(\text{Na Spline})^{*} - 17018{\cdot}74.\text{Na.Sr}^{*}$$

Na Spline as above

Strontium Effect in Predominantly Sodium Modified Samples *(see Figure 52)*

$$\text{AFS Modification \# Increment} = -815{,}218{\cdot}78.(\text{Sr Spline})^{*} - 17018{\cdot}74.\text{Na.Sr}^{*}$$

Sr Spline as above

8.2.2 Porosity

The following MLR results relate test-bar cross-sectional area porosity (%), to the sample composition (wt%). The full MLR outputs of the following relationships may be found in Appendix O2. It can be seen below that the R^2 values for the porosity expressions are 0.25 and 0.22 respectively; this indicates that the predictive worth of these functions is not very high. Whilst the MLR expressions only reduce the predictive error by 25% and 22% (R^2) compared to using the mean observed value, the influence of several elements has been established with statistical significance levels high enough to be irrefutable (p-value $<< 0.2$).

<u>Overall Porosity Equations</u>

Sodium Modified Samples

$$\%\ \text{Area Porosity} = 57{\cdot}1384.\text{Na}^{1.57*} + 1{\cdot}2631.\text{B}^{0.5*} + 0{\cdot}8965.\text{Mg}^{*} - 0{\cdot}0161.\text{Si} + 0{\cdot}2098$$

$$R^2 = 0{\cdot}25$$

Strontium Modified Samples

$$\% \text{ Area Porosity} = 0{\cdot}3720.B^{0.2*} + 1{\cdot}4169.Mg^{*} + 0{\cdot}2441.Mn^{*} - 67{\cdot}1101.Na^{*} + 1{\cdot}1126.Cu + 0{\cdot}0706$$

$$R^2 = 0{\cdot}22$$

The terms in the above expressions are listed in order of statistical significance with the silicon and copper terms being associated with only 70-80% certainty that they exist at all (*p* values 0.21 and 0.28 respectively). Since the existence of neither the silicon nor copper terms can be assured, these effects have not been illustrated. The silicon term was left in the sodium sample predictor set because, prior to adopting the sodium term in the $Na^{1.57}$ form, the beneficial effect of silicon was predicted as up to 90% certain. The strontium sample copper term was retained as MLR analysis of the full 495 sample observations indicated a beneficial copper term with 85% certainty and no significance could be associated with copper in the sodium modified observations.

Figures 53 through 56 illustrate the influence of sodium, magnesium, boron and manganese as given in the above results.

Boron

It can be seen (Fig. 53) that the two boron terms which seem completely different in the simple numerical results are in fact quite similar, with boron causing appreciable porosity increases in both the sodium and strontium modified samples. Statistically, the chances of boron not being detrimental are nil (0.001%) with the results suggesting that the bulk of the increased porosity occurs with very minor boron additions (i.e. > 0.01%).

As the boron addition took place via two distinctly different master alloys the full observation set was separated and analysed depending on which boron additive was used. The boron terms generated from this analysis (below and Figure 57) show quite clearly, that for a given level of boron, the propensity of a cast to form porosity is quite different depending on the boron additive used. The statistical significance of the two boron master alloy terms is extremely high, the lower of the two having a certainty of $8.5 \times 10^{-5}\%$ (*p*-value). Given the high significance of these two terms, it is probable that the predictive

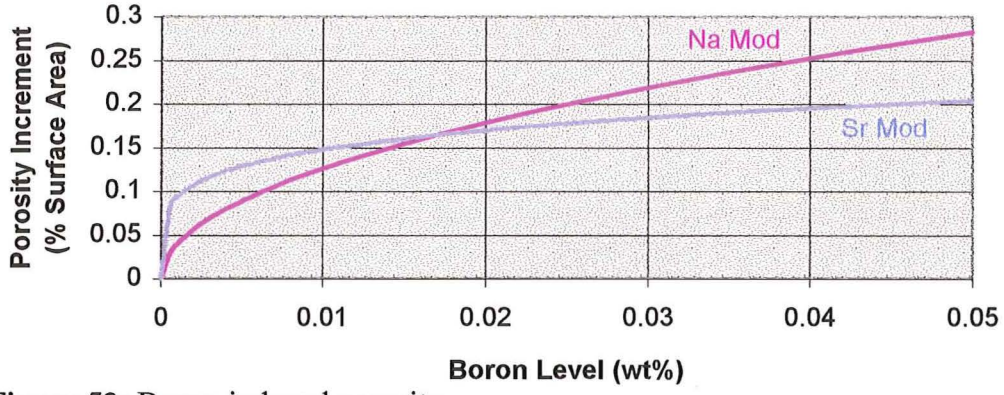


Figure 53: Boron-induced porosity.

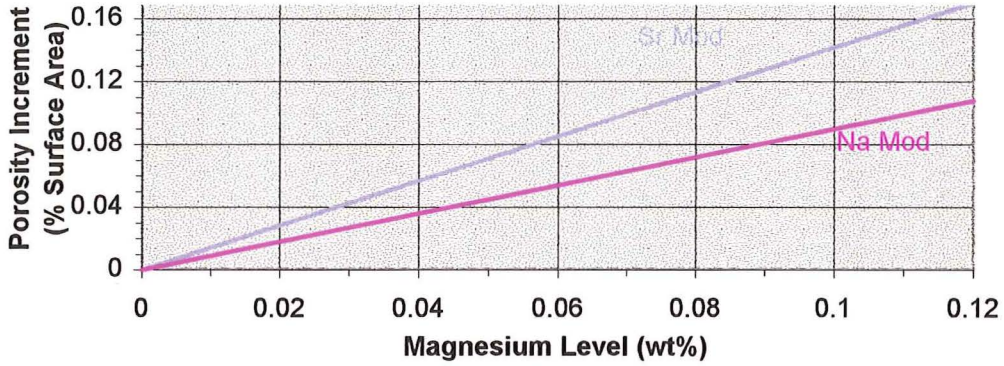


Figure 54: Magnesium-induced porosity increases.

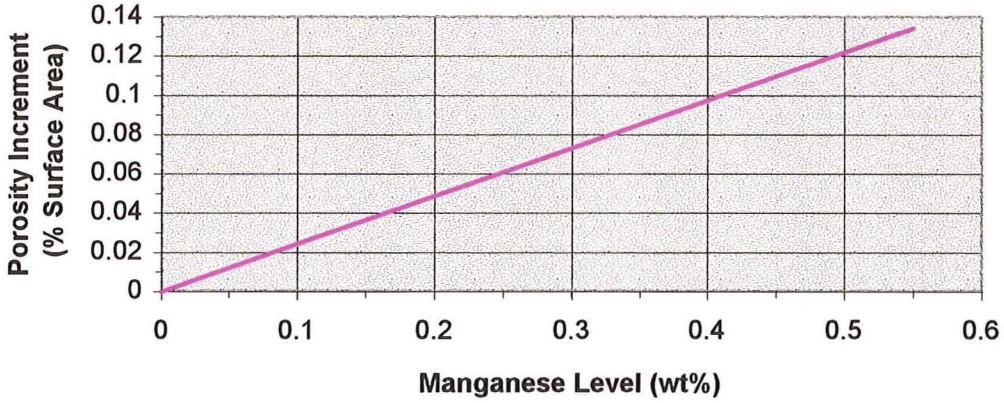


Figure 55: Manganese-induced porosity increases as found in strontium modified samples.

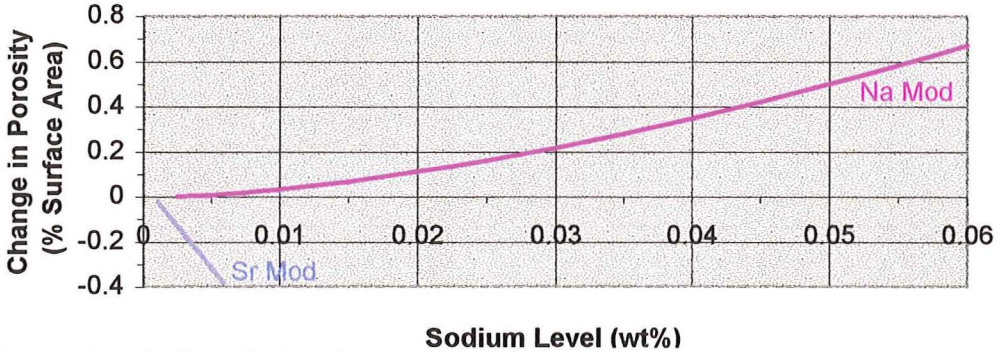


Figure 56: Sodium-induced porosity variation.

accuracy of the porosity expressions given above could be improved by substituting the quoted boron terms for the additive-dependent terms given below. The separated modifier data sets have not been reported in a regression form relative to the boron additive used, as the reduced observation sets produce overall MLR expressions of little significance due to the high variability associated with the porosity results.

Boron Additive Terms

3% Master Alloy Addition	$0{\cdot}4799.B^{0.27}$
5%Ti-1%B Master Alloy Addition	$0\cdot7338.B^{0.27}$

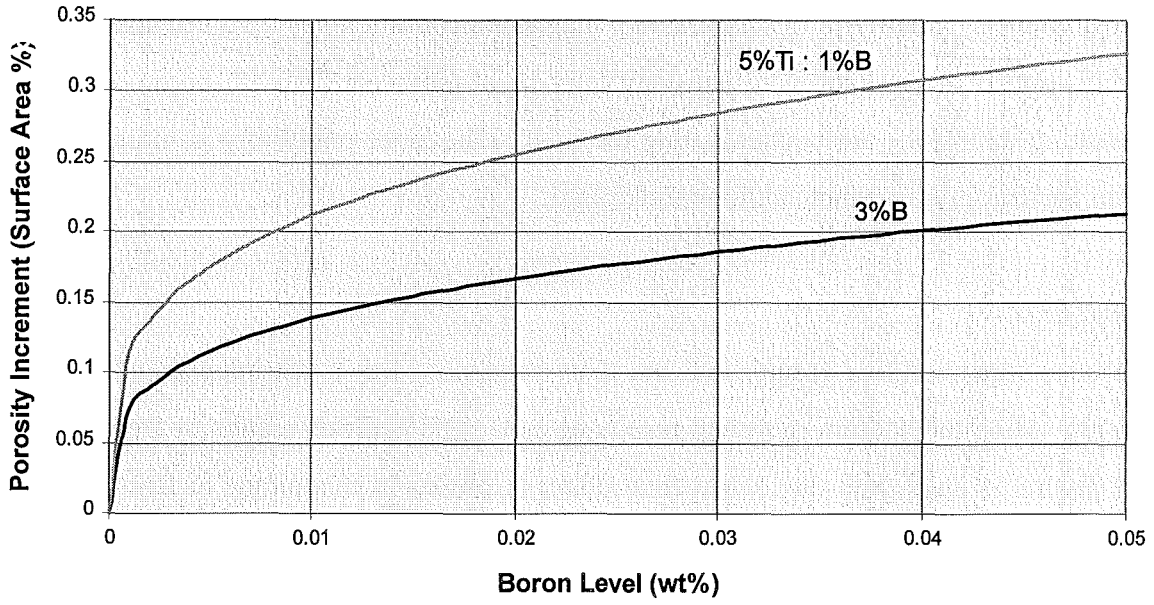


Figure 57: The effect of various boron additive forms on sample porosity.

Neither of the boron master alloys should have acted as direct sources of hydrogen thus the implication is that both master alloys introduced pore nucleants (inclusions). Since titanium is not implicated in the porosity results it must be concluded that the pore-promoting agents in the 5:1 alloy are primarily associated with the level of retained boron. It was not expected that the 5%Ti-1%B master alloy would induce ≈50% more porosity than the 3%B alloy, especially since the 5:1 alloy is specifically designed to introduce particles which are retained within final castings, while the AlB_{12} type Al-3%B alloy is intended to promote melt cleanliness via the deliberate introduction of inclusion formers which are ordinarily allowed to settle out.

Magnesium

The MLR results have revealed that magnesium has the effect of increasing porosity, slightly more so in the presence of strontium than with sodium (see Figure 54). Statistically, the least significant of the terms is that generated from the sodium modified samples; it being 98.8% certain that this term is indeed relevant. The likelihood of magnesium not increasing porosity in the strontium modified samples is one in 20,000 i.e. nil. These results highlight how the low predictive worth MLR porosity expressions still yield important and conclusive results.

Magnesium is known to increase hydrogen solubility[177] and thus theoretically to reduce porosity levels. Clearly in this case, either magnesium addition has involved simultaneous introduction of more hydrogen than may later be absorbed or, as with boron, additional nucleating inclusions are contaminating the melt, The latter possibility is more probable given the dry form in which addition took place.

Manganese

The strontium modified results indicate that manganese has a detrimental influence on porosity while the sodium modified results do not. The analysis results in Appendix O2 and Figure 55 show that this detrimental effect is similar in magnitude to that caused by magnesium and this coefficient is at least 99.7% certain within the bounds of the BS1490-LM6 composition range. The lack of a significant manganese term within the sodium modified results may be explained by sodium-induced porosity and variability overshadowing the effects of less influential elements. It is quite probable that the detrimental manganese effect occurs equally, irrespective of the modifier present.

Since manganese addition took place prior to degassing it is unlikely that much additional hydrogen, which may also have been introduced, would persist to later cause increased porosity. This indicates that either manganese promotes increased hydrogen adsorption or, directly or indirectly, increases pore nucleant density.

Sodium

Of all the elements investigated, sodium has by far the most pronounced influence on porosity. As shown in Figure 56, when sodium is the predominant modifier, the percentage of porosity area increases with increasing sodium content. When sodium levels

rise to 0.05%, porosity areas increase by 0.5%, an amount which is only matched by the maximum combined, boron, magnesium and manganese levels. At conventional sodium addition levels (0.015%) the porosity area increases by less than 0.1%, which is still of concern but no more so than the effects of the other quantified elements. When sodium is present as an impurity in strontium modified samples porosity levels decrease. This latter effect is difficult to explain but almost certainly occurs.

The large increases in porosity attributed to sodium modification may result from a number of sources. The most probable are: reaction with the atmosphere and oxide entrainment during the violent sodium/molten metal reaction; direct introduction of moisture via hygroscopic sodium reaction products or contamination from carried-over sodium storage oils. Each of the above pore sources were considered prior to casting and were minimised wherever possible.

The mechanics of the sodium introduction method do not seem at fault as this would occur irrespective of the actual addition amount and so be revealed as a step function as soon as increased sodium levels are recorded. The modification process itself also does not seem responsible for the increased porosity levels as no such effect was found with the use of strontium. It has been reported as recently as March 1995[178] that, as mentioned in Chapter 2, strontium is associated with increased porosity in Al-7%Si-Mg alloys and this occurs without appreciable variation in actual hydrogen levels. The failure of the results presented here to support this finding suggests that with the Al-Si eutectic alloy the influence of strontium (and hence modification) is not as pronounced as may otherwise be expected.

Other Elements

The influence of iron, silicon, titanium and strontium were either too variable or not significant enough to be detected via the porosity monitoring and MLR analysis methods used.

8.2.3 Hardness

The MLR results presented below relate the average Vickers hardness of each cast specimen (see Section 6.2) to the specimen composition. The percent area of porosity displayed by each test-bar has also been included as an independent variable (predictor).

Porosity was included as this property is poorly correlated to composition (see Section 8.2.2) and intuition suggests that porosity should have an important influence on recorded hardness. The full MLR hardness results are contained in Appendix O3. While being only 88% certain, the sodium-modification porosity term is the least significant in the given results. However, it is in excellent agreement with the strontium and full set porosity results which are up to 98.3% certain.

While the MLR results from both modifier data sub-sets and the full data set are presented overleaf, only the relevant modifier expressions are intended for predictive purposes. The full data-set results have been listed so as to indicate which predictor effects are invariant with regard to the modifier used, and hence have been illustrated using the full data set results. The hardness increments illustrated in Figures 58 through 63 may be regarded as increments from Hv 44.3, this being the predicted hardness of a sample containing 9.5% silicon with no other additives or impurities.

It should be noted that the trends influencing hardness bear no resemblance to those controlling tensile or proof strengths. This confirms that the approximations relating hardness and strength (often quoted by engineers and metallurgists alike) are not appropriate where cast Al-Si alloys are concerned.

Overall Vickers (Hv_{10}) Hardness Equations

Sodium Modified Sample Set

$$Hv_{10} = -0{\cdot}1371.(\text{Si Spline}) + 8{\cdot}1427.Fe + 26{\cdot}4430.Mg^{*} + 15{\cdot}3970.Ti^{*} + 4{\cdot}5961.Mn - 11{\cdot}9283.(Fe - 0{\cdot}05).Mn^{2} - 93{\cdot}6660.Ti.B^{*} - 0.5782{\cdot}Area + 15{\cdot}4718$$

$$R^{2} = 0{\cdot}84$$

$$\text{Si Spline} = Si^{2} - 31{\cdot}7.Si$$

Strontium Modified Sample Set

$$Hv_{10} = 42{\cdot}1925.Mg^{*} - 0{\cdot}09479.(\text{Si Spline}) + 7{\cdot}0974.Fe + 10{\cdot}4089.Ti^{*} + 6{\cdot}5447.Mn + 847{\cdot}384.(\text{Sr Spline})^{*} - 13{\cdot}1936.(Fe + 0{\cdot}05).Mn^{2} - 83{\cdot}2026.Ti.B^{*} - 0{\cdot}6520.Area + 22{\cdot}1689$$

$$R^2 = 0{\cdot}86$$

$$\text{Si Spline} = Si^2 - 34{\cdot}3.Si$$

$$\text{Sr Spline} = Sr^2 - 0{\cdot}093.Sr$$

Full Sample Set

$$Hv_{10} = 36{\cdot}2569.Mg - 0{\cdot}1213.(\text{Si Spline})^* + 7{\cdot}5862.Fe^* + 13{\cdot}3515.Ti - 47{\cdot}0602.Sr + 5{\cdot}8745.Mn^* - 121{\cdot}5768.Ti.B - 12{\cdot}3862.(Fe + 0{\cdot}05).Mn^{2*} + 13{\cdot}6706.B - 0{\cdot}6117.Area^* + 18{\cdot}4580$$

$$R^2 = 0{\cdot}83$$

$$\text{Si Spline} = Si^2 - 31{\cdot}8931.Si$$

Silicon

While the silicon spline coefficients listed in the MLR outputs may not seem compatible even at the 95% probability limits, this variability is almost entirely eliminated by the slightly different splines used. When the variation in each MLR silicon term was compared in the range 9.5-13.5%Si, the variation between the two modifier sub-set results was so small that the full-set spline and coefficient were selected for illustration in Figure 58.

Figure 58 clearly shows that as silicon levels rise, the hardness of the cast specimens also rises. This hardening effect reduces in magnitude as silicon levels increase but this is not very marked within the 9.5-13.5%Si range. If the displayed trends continue to higher silicon levels, then maximum hardness may be achieved with 15-17% silicon.

Magnesium

As is common among many of the properties monitored, the effect of magnesium was significantly different depending on which modifier was employed. In this case, magnesium hardening was nearly 70% more pronounced in the strontium modified samples than those containing predominantly sodium. In the former case a 0.1% increase in magnesium levels resulted in hardness increases of approximately 4.25 units while, in the latter, increases of only 2.5 units occurred (see Fig. 59). That magnesium has such a pronounced effect was unexpected and hard to explain as the magnesium phases present in

the cast microstructures were not abundant, nor did they appear to cause the microstructural changes which would be expected given the degree of hardening observed. Since magnesium was found to interact closely with the modifiers in both the tensile strength and modification MLR analyses, several Mg/modifier predictor variables were tried. However, none proved appropriate. An MLR analysis was also run on the samples containing no appreciable modifier; this failed to find a significant magnesium effect, so no justifiable trends could be established relating magnesium hardening effects to modification.

Strontium (and Sodium)

As Figure 60 shows, strontium had a softening effect on the cast microstructures. This softening was most pronounced with strontium levels between 0.035 and 0.06 percent, this corresponding to the region in which overmodification begins but prior to the formation of conspicuous Al_2Si_2Sr constituents. This suggests that strontium modification softens cast structures by an appreciable amount but this effect is arrested by the onset of overmodification and then reversed when strontium containing constituents become obvious within the cast microstructure (see Plate 21).

It could be assumed that the softening attributed to strontium results directly from variation in eutectic refinement. Indeed, the points at which arrest and reversion of the softening effect occurs seem to support this logical assumption. What complicates and effectively negates this possibility is the finding that eutectic refinement by sodium does not produce analogous results. Since sodium produces more pronounced eutectic refinement and overmodification it seems logical that hardness variations associated with sodium should be of at least the same magnitude as those due to strontium. If sodium had effects similar in magnitude to strontium, the sodium sample MLR should have detected this as it did the titanium and manganese terms, which are of comparable magnitude. The failure to establish a sodium term at any level of statistical significance suggests that the effect of this element and hence eutectic refinement is minimal and that strontium related softening occurs for reasons which remain unknown and in need of investigation.

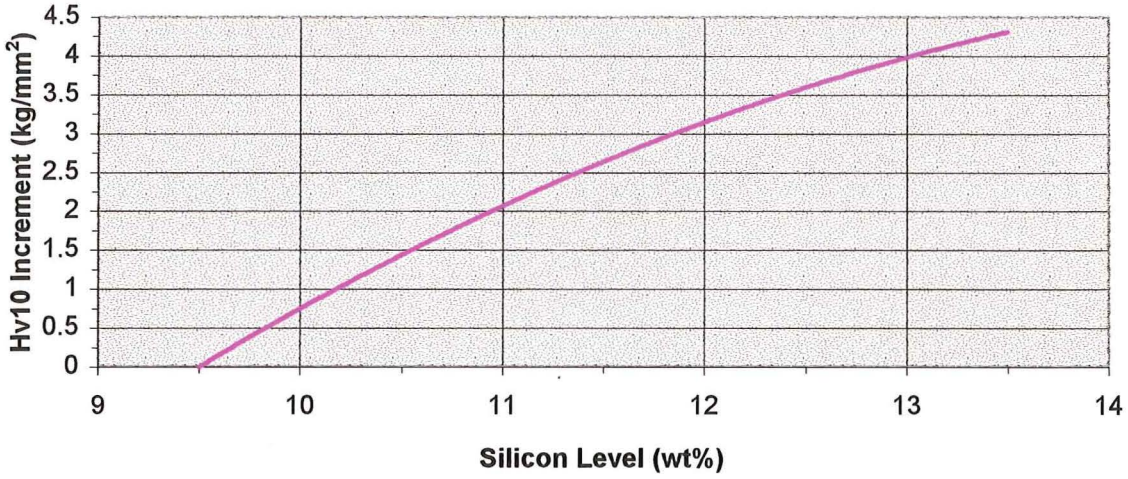


Figure 58: The effect of silicon on the Vickers Hardness of sand-cast Al-Si eutectic alloy.

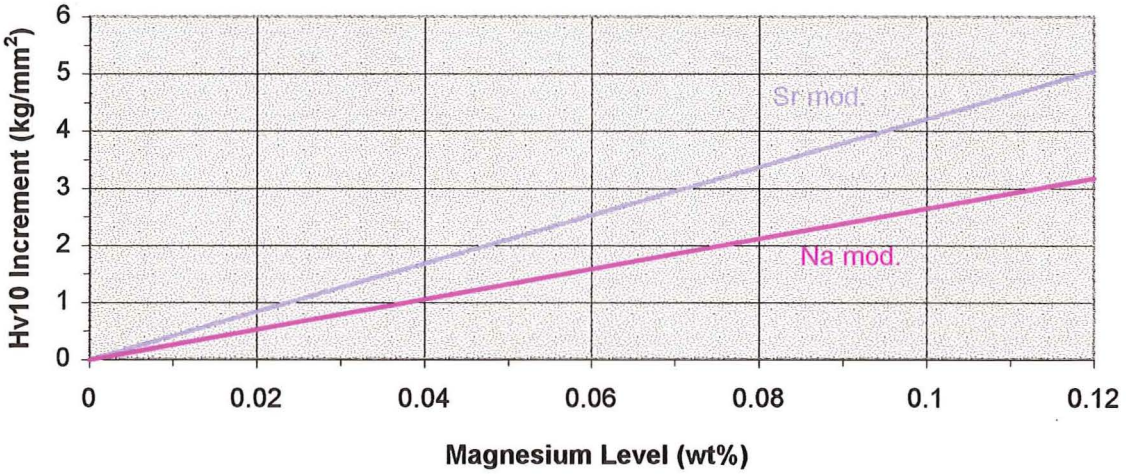


Figure 59: The effect of magnesium on the Vickers Hardness of sand-cast Al-Si eutectic alloy.

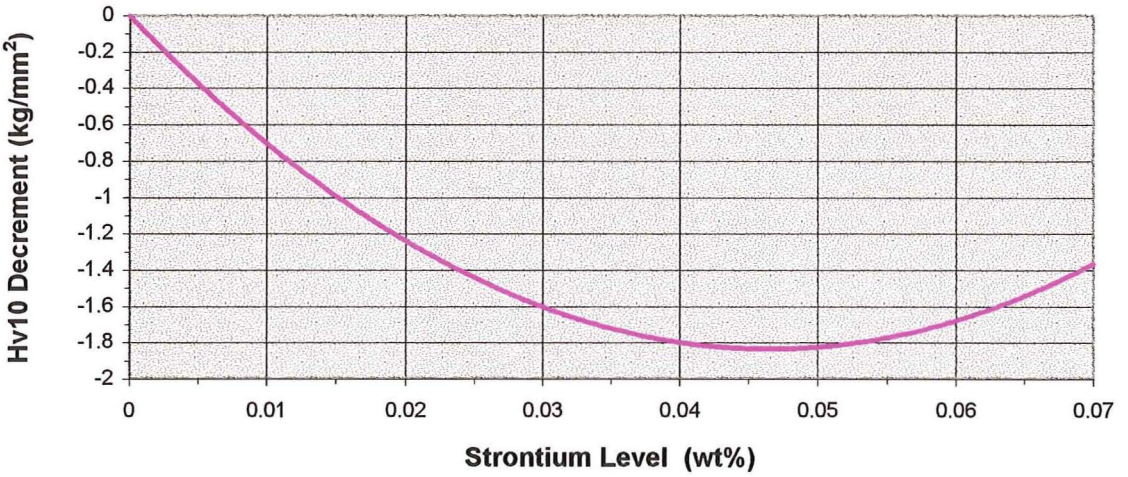


Figure 60: The softening effect of strontium on sand-cast Al-Si eutectic alloy.

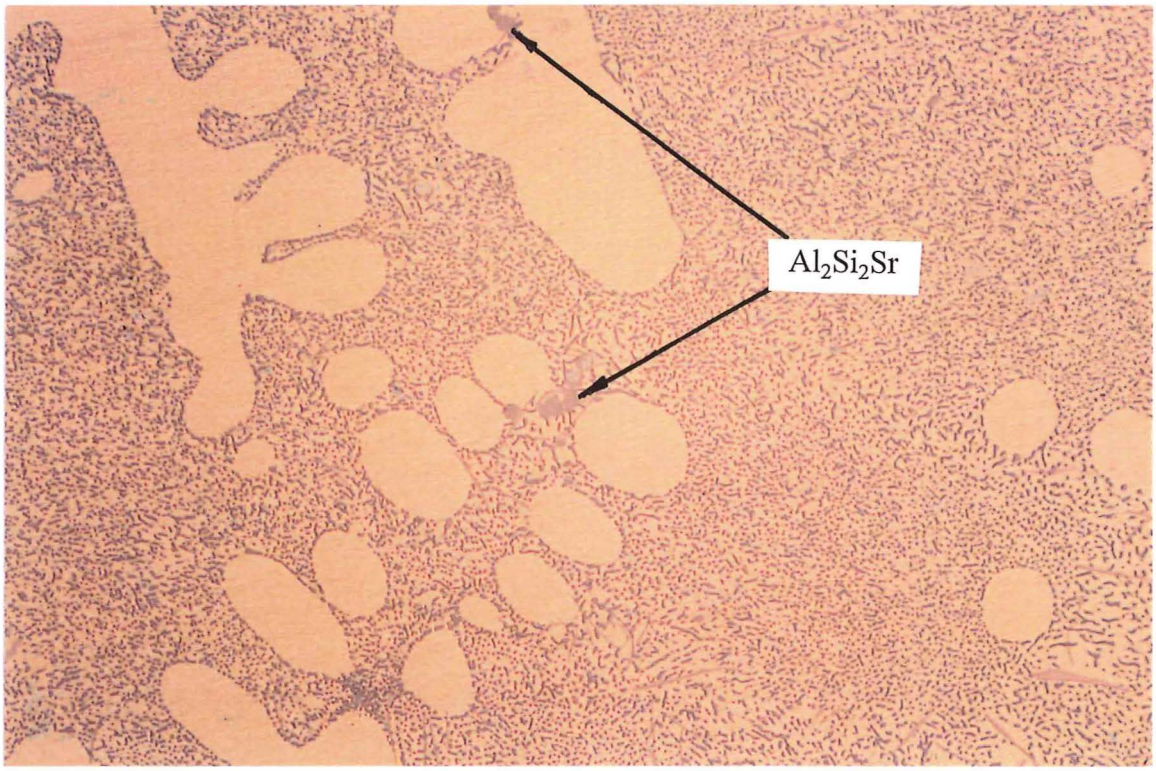


Plate 21: Strontium constituents in a strontium-overmodified structure, sample 182-2-115 (x114).

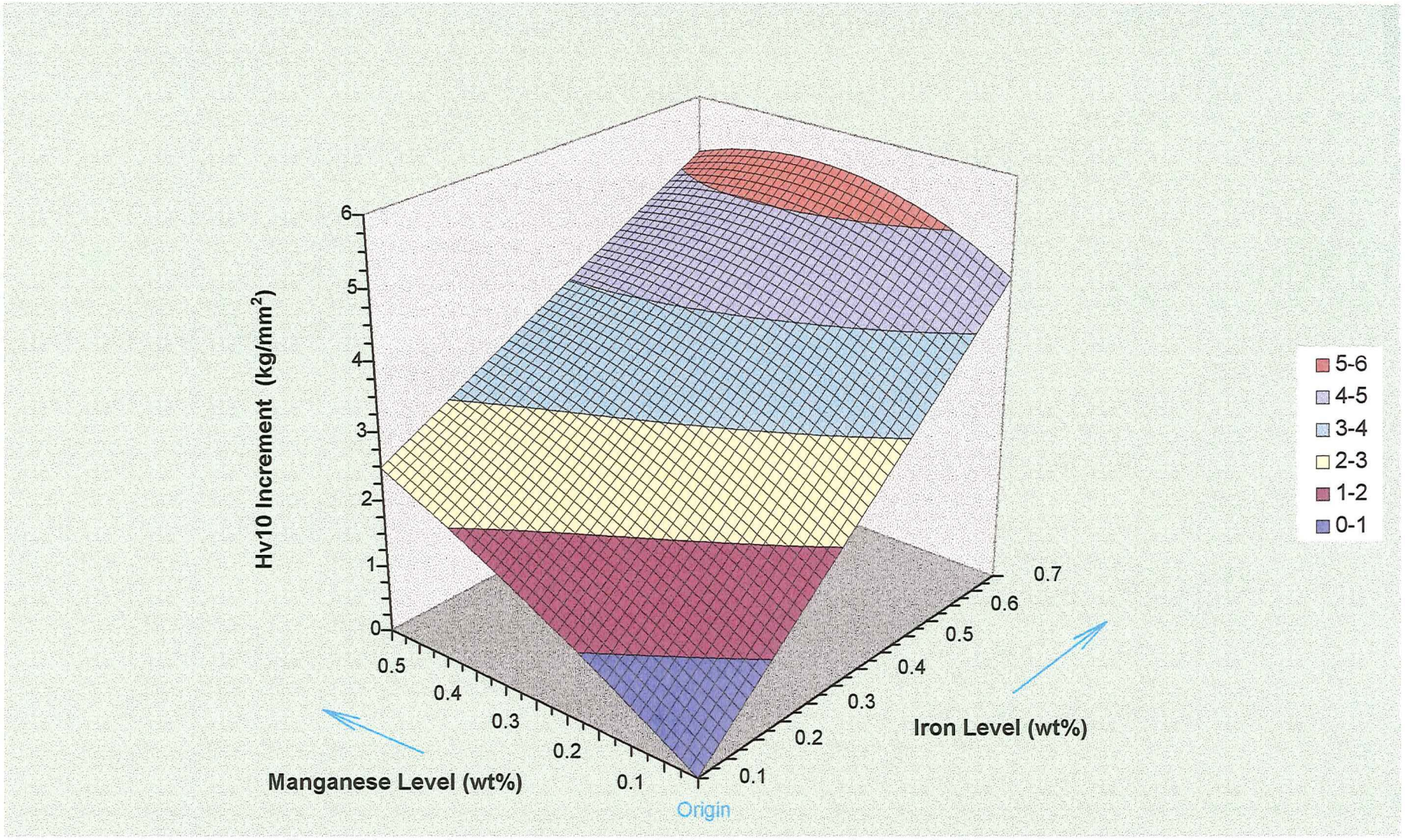


Figure 61: The hardening effects of iron and manganese as revealed by the MLR analysis -c.f. Figure 94.

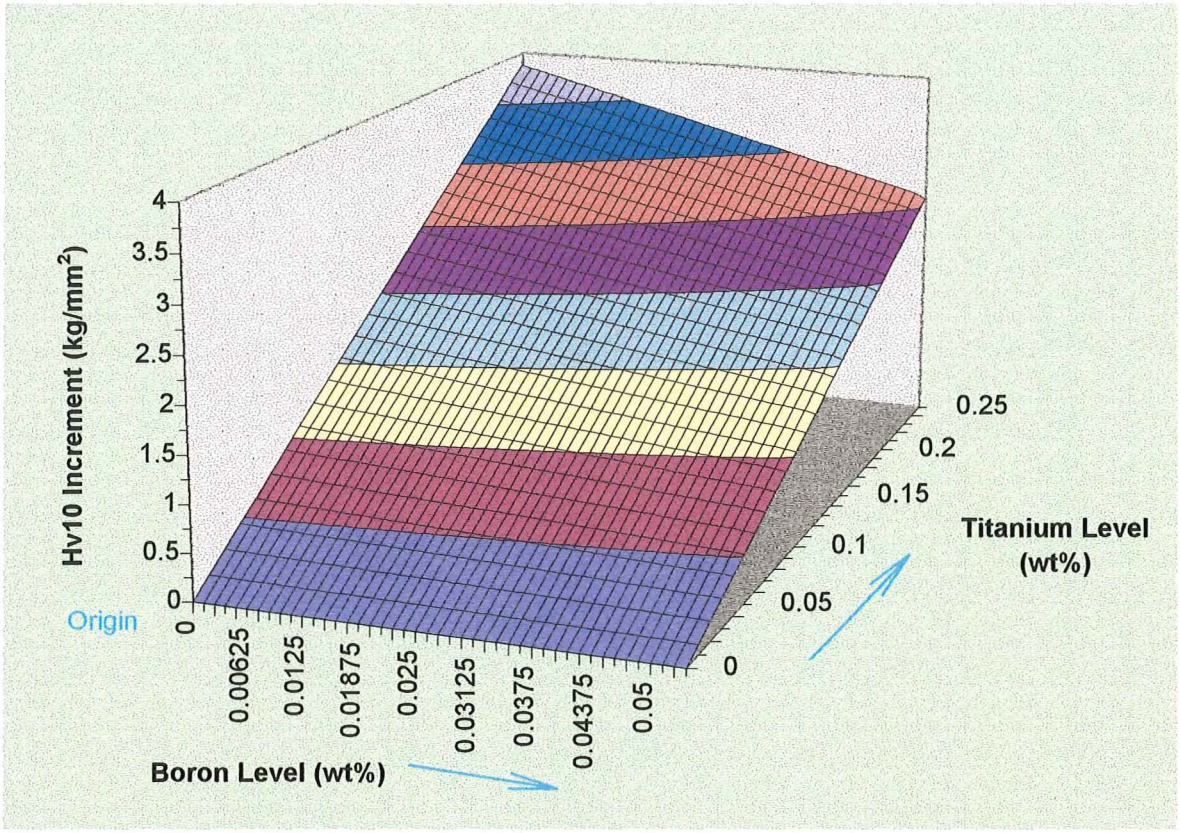


Figure 62: The effects of titanium and boron on the Vickers Hardness of sodium modified sand-cast Al-Si eutectic alloy.

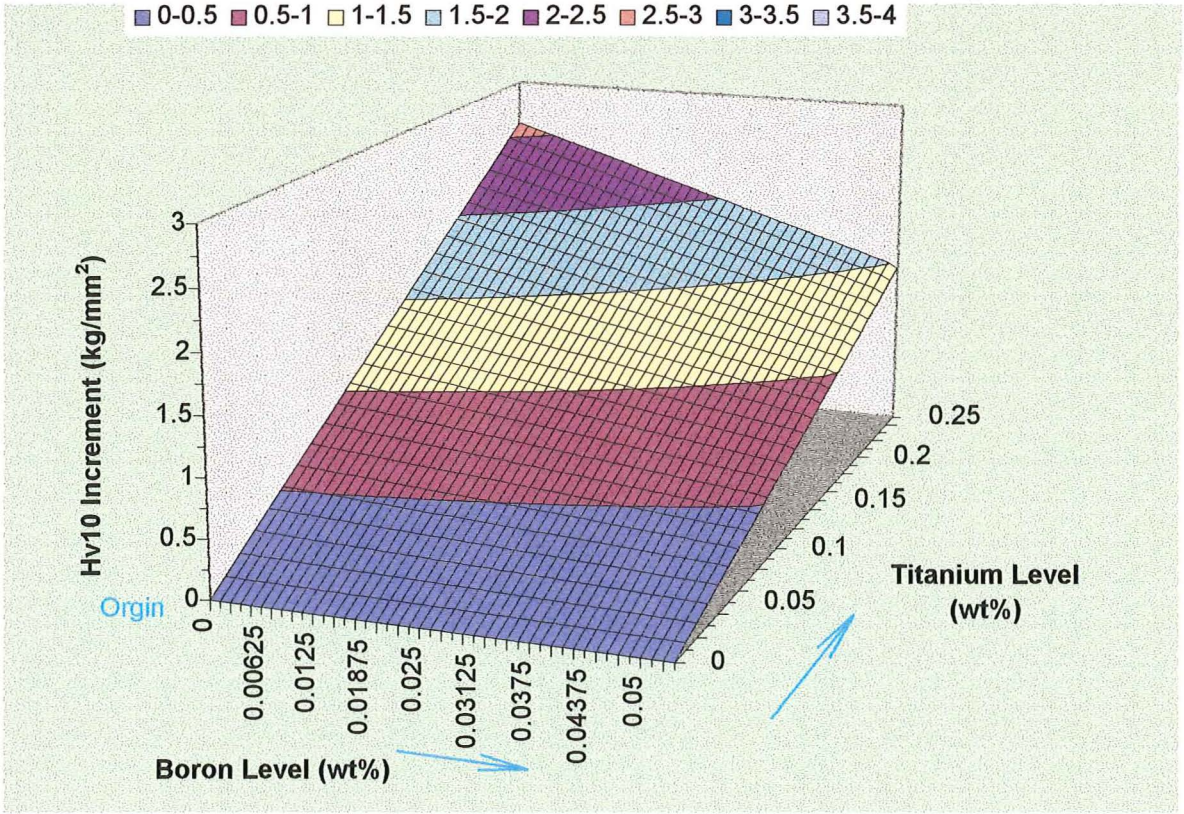


Figure 63: The effects of titanium and boron on the Vickers Hardness of strontium modified sand-cast Al-Si eutectic alloy.

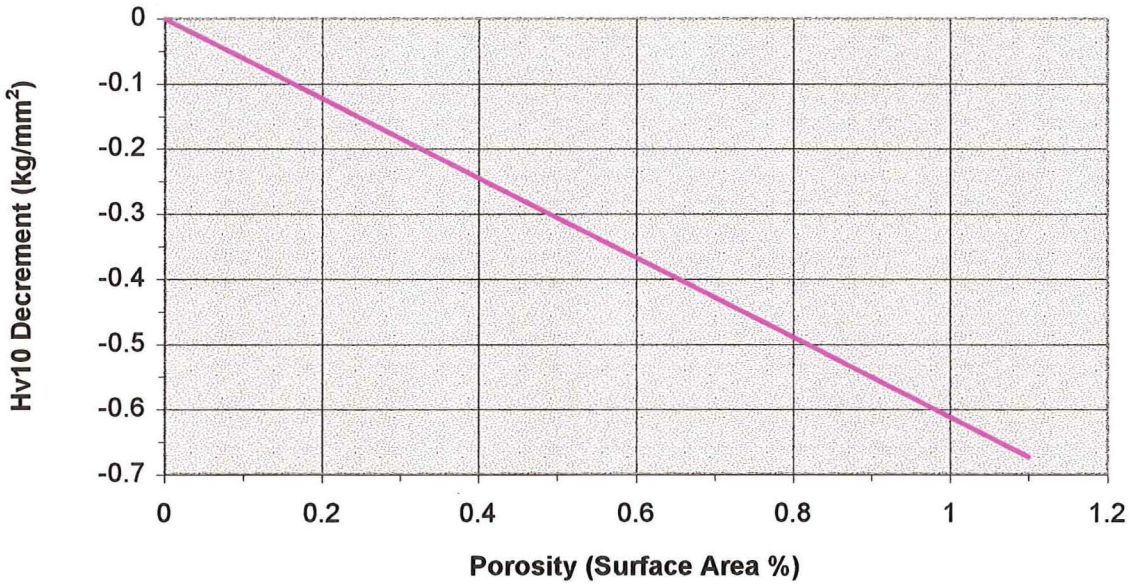


Figure 64: The effect of porosity on the Vickers Hardness of sand-cast Al-Si eutectic alloy.

Iron and Manganese

Both iron and manganese effects are largely unaffected by modification, irrespective of the modifier used or the apparent level of modification. As illustrated in Figure 61, each of these elements cause substantial hardening, although the effects of the two in combination are not truly additive. At high manganese levels, i.e. >0.3%, the hardening due to iron appears to be reduced some 60-65%. Similarly, at low iron levels (0.1%) a 0.5% increase in manganese content increases hardness 2.5 kg/mm^2, while at 0.6% iron hardening due to manganese peaks at only 0.8 kg/mm^2 - this corresponding to 0.3% Mn, not the 0.5% limit investigated.

The possible reasons as to why iron and manganese display the trends shown in Figure 61 will be covered in detail in Section 8.3.

Titanium and Boron

As Figures 62 and 63 show, the effects of titanium and boron are influenced by which element is used to perform modification. The hardening effect of titanium and the softening effect of boron are approximately 50% higher in samples modified with sodium than those utilising strontium. This corresponds to 0.25% titanium causing $\approx$ 1 kg/mm^2 more hardening in a sodium modified sample than in a similar strontium modified sample. The hardness regression performed on the unmodified sample data failed to produce a significant Ti or B term, hence it is impossible to judge whether modification or the modifying elements are responsible for the disparity between the sodium and strontium sample results.

While boron is shown as having a minimal effect at low Ti levels in each of the individual modifier MLR results, when the full 495 observations are processed it is shown to have a slightly positive effect (with 99.5% certainty). With no titanium present, the full observation analysis suggests that a 0.05% boron increase causes a 0.7 kg/mm^2 *increase* in hardness. Irrespective of the samples analysed, when 0.25% titanium is present, 0.05% boron *reduces* hardness by around 1 kg/mm^2.

Porosity

Since porosity had been shown to have poor correlation with sample composition it was known that an MLR analysis relating hardness and composition would not account for this

suspected source of hardness variability. Accordingly, by including porosity levels as a predictor variable, it was hoped that the otherwise unexplainable error would be reduced thus improving the sensitivity with which remaining predictors could be established. As was expected, the effect of porosity is negative and independent of the level of modification or modifier used. The actual magnitude of the porosity effect was smaller than expected, being virtually insignificant (0.05 kg/mm^2) at the porosity levels encountered in most cast specimens (>0.1%). As Figure 64 shows, even with samples displaying gross porosity (>1.0%), the average hardness dropped by less than 0.7 kg/mm^2. Although porosity had less influence than anticipated, it was retained as a predictor variable as the MLR porosity terms displayed no indication of being a source of error due to collinearity.

8.2.4 Grain Size

The MLR results shown below relate ASTM macro-grain size number to sample composition (wt%).

Overall Grain Size Equation

$$\text{ASTM G(M)} = 32{\cdot}1848.B^{0.5\clubsuit} - 67{\cdot}4788.(Ti.B)^{0.45\clubsuit} + 19{\cdot}7787.Ti^{\clubsuit}$$
$$- 0{\cdot}0420.(Si^2 - 26{\cdot}09.Si)^{\clubsuit} - 0{\cdot}7836.Mn + 17{\cdot}3521.Na - 6{\cdot}92630.Sr + 0{\cdot}3257$$

$$R^2 = 0{\cdot}743$$

The independent variables above are listed in order of statistical significance with the boron term significant to the 4×10^{-114}% level and the strontium term to the 4% level (two tailed *t*-test). It can be seen that the above expression does not vary between the types of modifier used. Depending on the modifier used, variations in the influence of boron and manganese were encountered. However, the boron variation was minor and the apparent variation with manganese was difficult to substantiate as the statistical significance of the strontium-manganese effect was relatively low.

Titanium and Boron

The theory and previous experimental findings discussed in Section 2.3 suggest that titanium and boron act in a synergistic manner; the results of this study do not support this assumption (as shown in Figure 65). When considered separately boron acts as a much stronger grain refiner than titanium. At low titanium levels (below 0.08%) grain refinement is greatly improved by the addition of boron however the presence of titanium at these levels seems only to hinder the action of boron alone. At higher titanium levels (above 0.08%) the refining action of titanium dominates and the addition of as little as 0.01% boron reduces the refinement to levels similar to that achieved with 0.08% titanium alone.

To highlight any variation in the grain refinement response as a function of the form in which titanium was added (compacted powders or 5%Ti-1%B master alloy), a separate MLR analysis was carried out on only those samples not containing boron. The titanium coefficient resulting from this analysis was 19.08 compared to 19.78 when all samples are analysed. The difference in these terms amounts to 0.14 ASTM G(M) units at 0.2%Ti - an insignificant, amount indicating that the influence of the added titanium was virtually independent of the addition form.

Since boron had been added using either the 3%B alloy, the 5%Ti-1%B alloy or a mixture of the two, it was conceivable that the boron effects would vary depending on the additive used (This possibility was compounded by the knowledge that the 3%B alloy was not of the intended type - see section 5.2). A plot was created relating the MLR residual values to the recorded boron level according to the type of addition used- see Figure 66. This plot reveals no significant trends, which leads to the conclusion that boron from the 3%B master alloy was just as effective as that derived from the 5%Ti-1%B alloy.

Sodium and Strontium

As illustrated in Figure 67, the modifiers have a very minor effect upon the grain size especially considering that they are usually present in levels no higher than 0.03%. Initially it was assumed that both modifiers would have a similar effect. But, as shown in Figure 66, sodium tends to refine the grain size while strontium coarsens it. Of the two

terms, lower statistical significance is associated with the strontium effect; even so, this term is significant to the 4% level.

The sodium term included in the above MLR equation came from analysing all 495 samples. When only the sodium samples are analysed the sodium coefficient increases slightly to 20.14. The difference between these factors is of little practical importance, amounting to less than 0.05 G(M) ASTM units for a typical sodium level (0.015%). This difference is smaller than could reasonably be measured. The strontium factor was consistent to within 0.3% regardless of whether all samples or simply those containing strontium were analysed (see Appendix O Section 4).

Silicon

Apart from the traditional grain refiners, silicon was the element found to have the greatest effect on grain size (see Figure 68). As could be expected, the finest grain sizes were associated with 12.5-13.5%Si, this corresponding to the compositions at which aluminium dendrites cease to be observed and eutectic cells become more predominant. Interestingly, samples displaying eutectic cells as the defined grains were not highlighted as inconsistent when compared to the remaining analysis results. This implies that eutectic cells are refined in the same manner as are aluminium dendrites. This assumption, while seeming valid, has little foundation as very few samples displayed fully hypereutectic structures due to the eutectic shift being dominated by modifier addition.

Manganese and Other Elements

No influence of either iron or magnesium on grain size could be detected. However, manganese was exposed as being a detrimental impurity. The statistical significance of the manganese factor used in the above equation is 0.17%, which comes from analysis of 493 observations. When sodium and strontium samples are analysed independently, it appears that the manganese is three times more detrimental in the presence of sodium than it is with strontium. As mentioned above, this is difficult to substantiate statistically. The effect of manganese as indicated by the full analysis is shown in Figure 69.

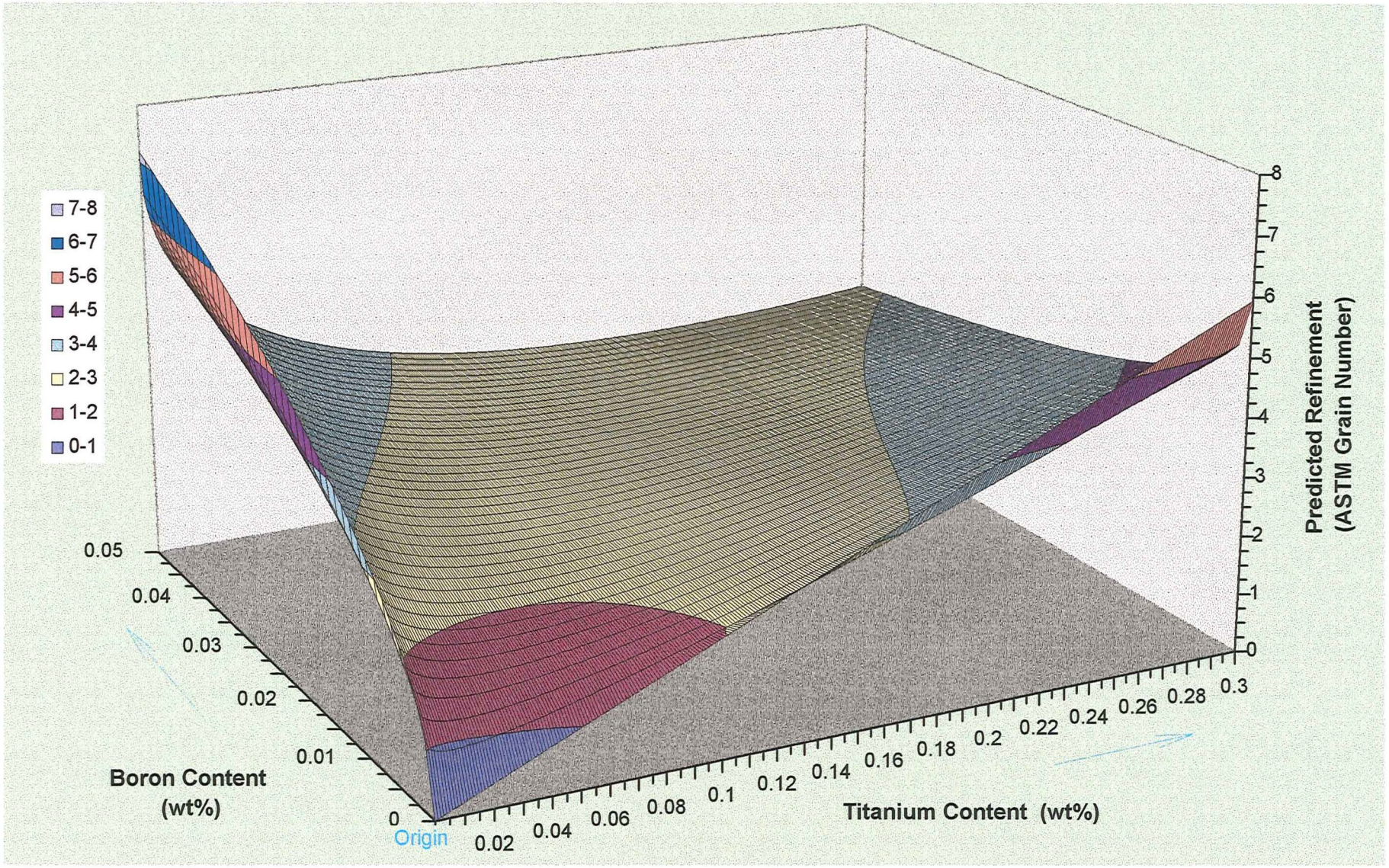


Figure 65: The MLR-derived titanium-boron grain refinement interaction surface.

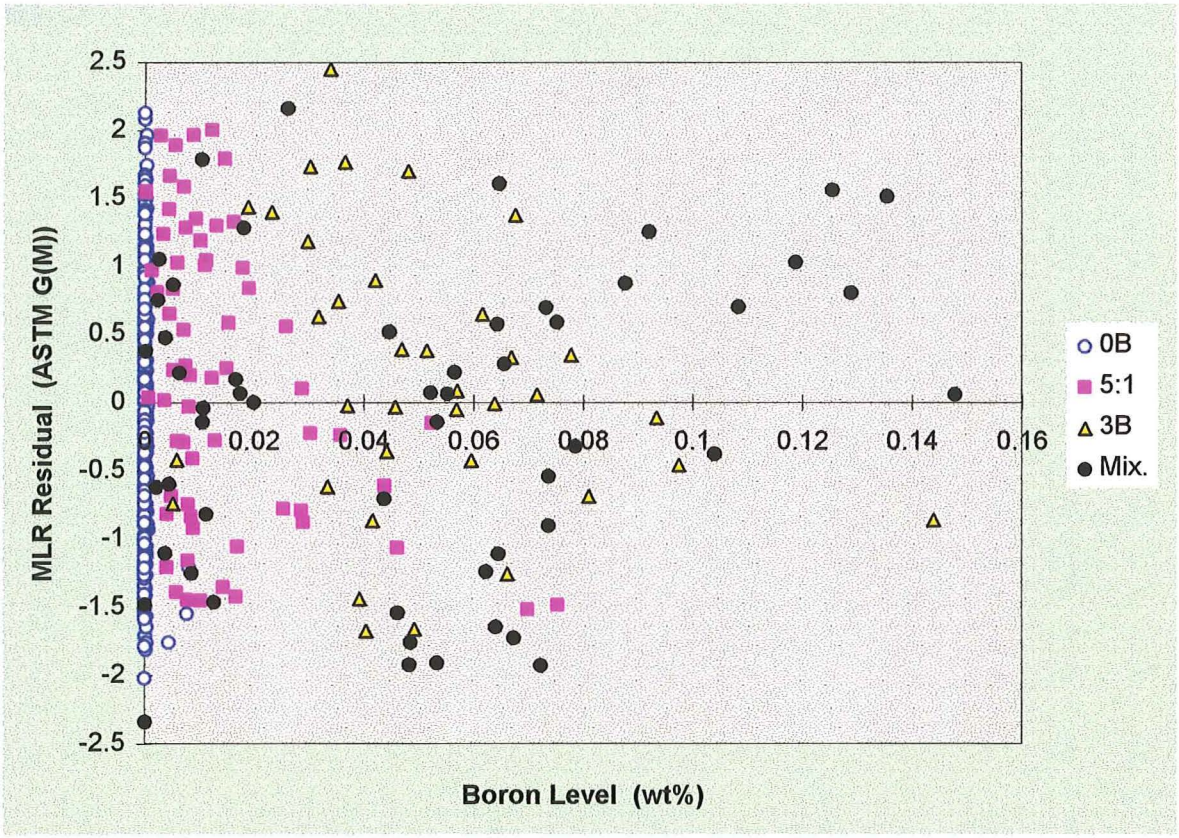


Figure 66: The variation in MLR grain size residuals depending on the boron additive used.

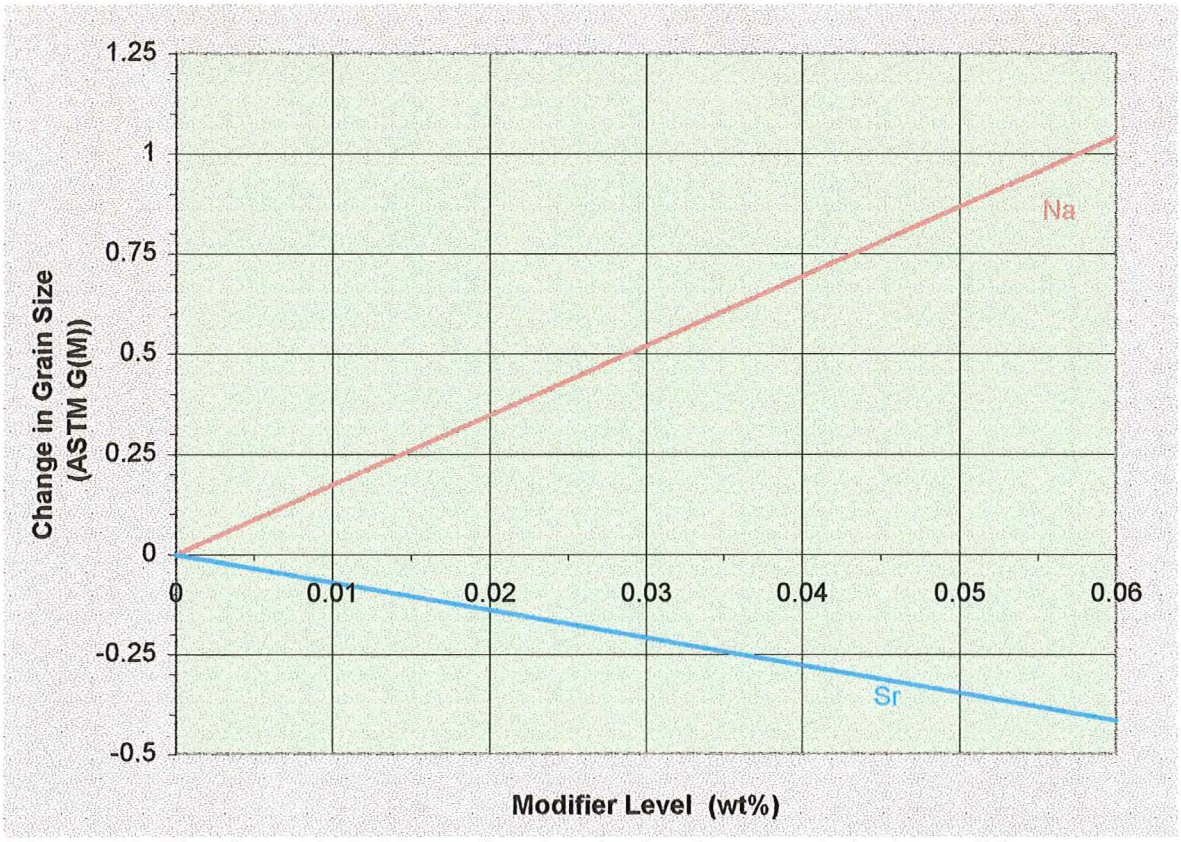


Figure 67: The change in MLR predicted grain size due to variationin modifier content.

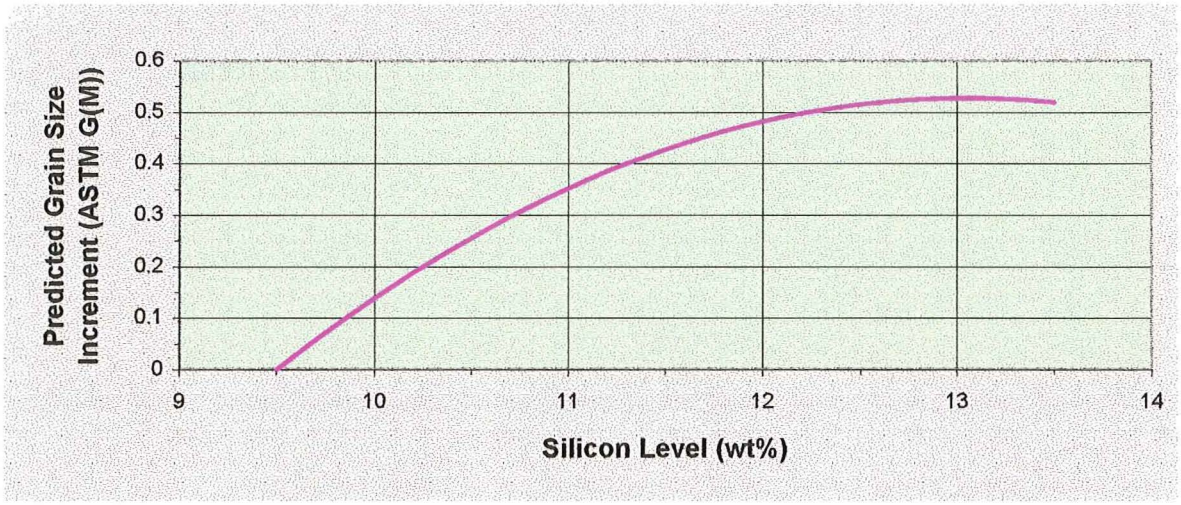


Figure 68: The change in predicted grain size due to silicon variation.

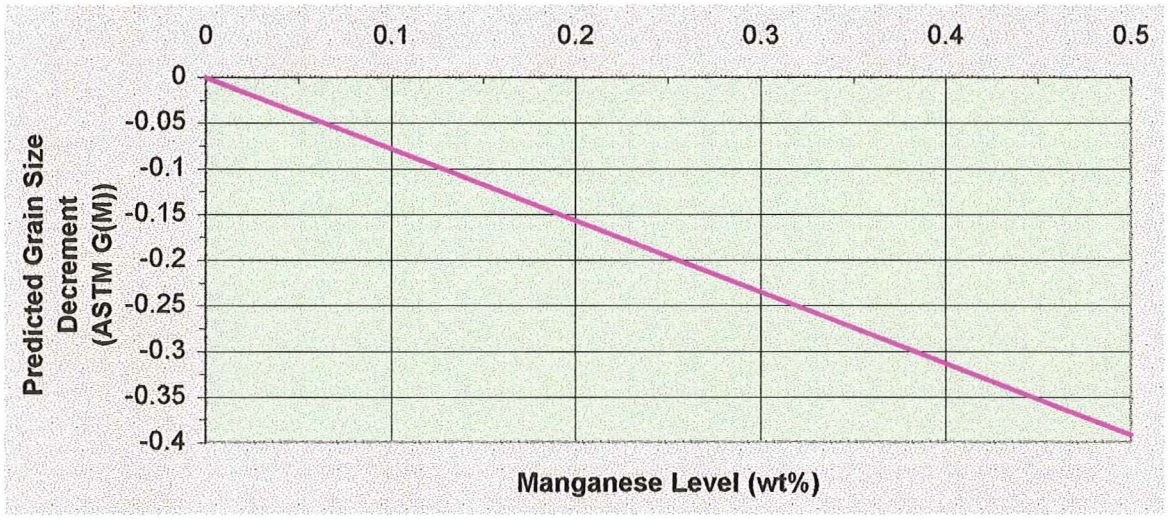


Figure 69: The change in predicted grain size due to manganese variation.

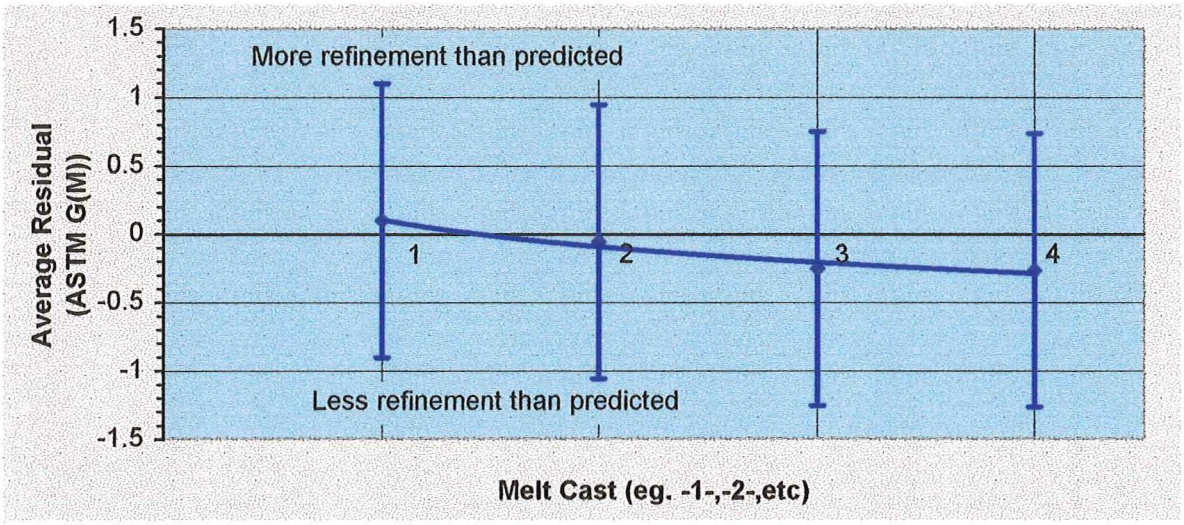


Figure 70: The dependence of recorded average grain size on cast number.

Grain Refiner Fade

The effects of conventional grain refiners fade with time due to either dissolution or sedimentation and therefore it was possible that regression analysis based on the composition at the time of casting may have been inappropriate. Optimum melt exposure times for each of the refiner additives were unknown and so problems may have been encountered due to variation in grain refiner response as a result of the order in which specimens were cast within a single melt. This potential problem was assessed by separating and plotting the average MLR-generated residual for each of the four possible melt casts. As Figure 70 shows, optimal refinement is associated with the first cast with subsequent casts displaying decreasing refinement levels below those predicted by the MLR expression. As shown by the standard deviation error ranges of the average grain size residuals, it is quite possible that no fade occurs, or that refinement actually improves with time. The average fade is approximately 0.4 ASTM G(M) units between the first and fourth cast specimens. Using the above findings to modify the regression analysis technique, or to devise fade-compensating additions for samples cast after the first pour, was not viable due to the calculated fade being too small for conclusive findings to be reached. This finding verifies that errors introduced by the assumption that grain refinement would be independent of grain refiner exposure time, were not large enough to significantly effect the MLR results.

8.2.5 Tensile Properties

The ten MLR analysis outputs on which the following results are based are included in Section Five of Appendix O. The effects of each element on a specific property, are summarised in the following figures and have been selected from the various MLR outputs based on the possible error and statistical significance of each predictor term. For example, the effect of iron on 0.2% proof strength is independent of the modifier used, hence the most statistically significant coefficient suitable for illustration is derived from the full sample set analysis. The alternative situation is encountered with the proof strength modifier coefficients as in this case, large variations in the modifier coefficients occur depending on which modifier data-set is analysed. The analysis based on the full sample set displays the most statistically significant sodium term but the less significant term,

derived from analysing the sodium-containing samples only, is more appropriate for illustration because it is not subject to errors such as heteroscedasticity which may be introduced by the strontium containing samples. As in the previous MLR expressions terms which have been selected for illustration are denoted by a club (♣) symbol.

The property increments displayed in Figures 71-89 may be combined with the following base properties:

T.S.	117 MPa
0.2%P.S.	75 MPa
δL	7.1%.

These properties represent the MLR-predicted properties of an aluminium alloy containing 9.5% silicon with no other elements present (hence, this is the composition from which the following figures start). It should be noted that the MLR results for the sodium sample set do not predict the above base TS until sodium levels reach 0.002%. This is thought to be due to inaccuracies in the sodium spline when applied to the lower limits of the observation data (0 - 0.003%Na). The sodium property variations displayed in Figure 74 have been corrected so that the above base properties may be applied.

Overall Tensile Strength Equations

Full Sample Set

$$TS\ (MPa) = 1{\cdot}0608.(Na\ Spline)^{\clubsuit} + 1{\cdot}3845.(Sr\ Spline)^{\clubsuit} - 263268{\cdot}68.(Na.Sr)^{\clubsuit} - 0{\cdot}6841.B + 33{\cdot}3912.Ti - 1{\cdot}5900.Mg.(Na\ Spline.\ Sr\ Spline) - 1{\cdot}8154.(Si\ Spline) + 3{\cdot}3363.Fe - 40{\cdot}7611.((Fe + 0{\cdot}325).(Mn + 0{\cdot}05))^2 + 14{\cdot}8869.Mn - 122{\cdot}2308$$

$$R^2 = 0{\cdot}68$$

$$Na\ Spline = 1{,}562{,}216{,}460{\cdot}99.Na^5 - 302{,}724{,}433{\cdot}82.Na^4 + 21{,}878{,}711{\cdot}9.Na^3 - 720{,}994{\cdot}1.Na^2 + 10{,}161{\cdot}01.Na$$

$$Sr\ Spline = 176{,}630{\cdot}16.Sr^3 - 30{,}116{\cdot}56.Sr^2 + 1{,}414{\cdot}5.Sr$$

$$Si\ Spline = Si^2 - 22{\cdot}5.Si$$

Sodium Modified Sample Set

$$TS\ (MPa) = 1{\cdot}05162.(Na\ Spline)^{*} - 2{\cdot}6709.(Si\ Spline)^{*} + 20{\cdot}0576.Fe^{*} - 1{\cdot}3458.Mg.(Na\ Spline)^{*} - 54{\cdot}3492.((Fe + 0{\cdot}325).(Mn + 0{\cdot}05))^{2*} + 15{\cdot}459.Ti^{*} - 97{\cdot}1074.B^{*} + 9{\cdot}7089.Mn^{*} - 243{\cdot}975$$

$$R^2 = 0{\cdot}74$$

$$Na\ Spline = 1{,}562{,}216{,}460{\cdot}99.Na^5 - 302{,}724{,}433{\cdot}82.Na^4 + 21{,}878{,}711{\cdot}9.Na^3 - 720{,}994{\cdot}1.Na^2 + 10{,}161{\cdot}01.Na$$

$$Si\ Spline = Si^2 - 23.Si$$

Strontium Modified Sample Set

$$TS\ (MPa) = 1{\cdot}1052.(Sr\ Spline)^{*} - 140{\cdot}2382.B^{*} + 28{\cdot}5073.Mn^{*} + 35{\cdot}4113.Ti^{*} - 3{\cdot}165.Mg.(Sr\ Spline)^{*} - 48{\cdot}9413.((Mn + 0{\cdot}05).(Fe + 0{\cdot}325))^{2*} + 12{\cdot}2760.Fe^{*} - 0{\cdot}5019.(Si\ Spline)^{*} + 62{\cdot}4495$$

$$R^2 = 0{\cdot}67$$

$$Sr\ Spline = 176{,}630{\cdot}16.Sr^3 - 30{,}116{\cdot}56.Sr^2 + 1{,}414{\cdot}5.Sr$$

$$Si\ Spline = Si^2 - 20.Si$$

Non-Modified Sample Set

$$TS\ (MPa) = -21{\cdot}0286.Fe^{*} + 36{\cdot}7897.((Fe + 0{\cdot}325).(Mn + 0{\cdot}05))^2 + 116{\cdot}3912.Mg^{*} - 2{\cdot}7128.Si^{*} + 39{\cdot}0806.Ti^{*} - 109{\cdot}9881.B + 148{\cdot}8920$$

$$R^2 = 0{\cdot}85$$

While the above regression is based on only 23 sample observations, the overall expression is significant to the 0.001% level and the least significant term is significant to the 3% level and in close agreement with the findings of the larger analysis results given above.

Overall 0·2% Proof Strength Equations

Full Sample Set

$$0{\cdot}2\%PS\ (MPa) = 22{\cdot}0573.Fe^{*} - 1{\cdot}1252.(Si\ Spline)^{*} + 277{\cdot}9991.Na + 25{\cdot}0473.Mg^{*} - 43{\cdot}2720.B - 95{\cdot}9459$$

$$R^2 = 0{\cdot}15$$

$$Si\ Spline = Si^2 - 25{\cdot}48.Si$$

Sodium Modified Sample Set

$$0{\cdot}2\%PS\ (MPa) = 24{\cdot}0262.Fe - 1{\cdot}3730.(Si\ Spline) + 205{\cdot}088.Na^{*} + 23{\cdot}3316.Mg - 135{\cdot}155$$

$$R^2 = 0{\cdot}16$$

$$Si\ Spline = Si^2 - 25{\cdot}5.Si$$

Strontium Modified Sample Set

$$0{\cdot}2\%PS\ (MPa) = 20{\cdot}1943.Fe - 0{\cdot}9880.(Si\ Spline) + 112{\cdot}8849.Sr^{*} - 64{\cdot}3248.B^{*} - 1847{\cdot}7415.Na + 6{\cdot}7393.Mn - 74{\cdot}7072$$

$$R^2 = 0{\cdot}16$$

$$Si\ Spline = Si^2 - 25{\cdot}5.Si$$

When compared to using mean proof stress values, the above R^2 values show that the 0·2% Proof Stress equations only reduce predictive errors by 15-16%. Since proof strength was measured with some accuracy and was thought to vary predominantly due to composition variation, these low R^2 values were not expected. As the substantial proof strength variations observed could not be explained by the influence of the main composition variables, several of the other monitored element levels were tried in the regression process however; none proved statistically significant. Whilst not being particularly enlightening for proof strength forecasting, the above relationships establish the effects of several addition elements.

Overall Ductility Equations

Full Sample Set

$$\delta L(\%) = -26{\cdot}4524.Mg - 7{,}232{,}685{\cdot}43.(Na\ Spline) - 5{\cdot}0349.Fe - 0{\cdot}0718.(Si\ Spline)^{*} + 18{,}800{\cdot}7.(Sr\ Spline) - 4{\cdot}0529.B^{0.3} + 194{\cdot}3701.((Fe - 0{\cdot}35).Mn)^{3} + 53{\cdot}5698.Ti.B - 19{,}469{\cdot}9391.Sr.Na - 2{\cdot}7302.Ti + 4{\cdot}8837$$

$$R^2 = 0{\cdot}74$$

$$Sr\ Spline = Sr^3 - 0{\cdot}174282.Sr^2 + 0{\cdot}00898221.Sr$$

$$Na\ Spline = Na^4 - 0{\cdot}140974401.Na^3 + 0{\cdot}00663617.Na^2 - 0{\cdot}000122504.Na$$

$$Si\ Spline = Si^2 - 12{\cdot}75Si$$

Sodium Modified Sample Set

$$\delta L(\%) = -7{,}493{,}267.(Na\ Spline)^{*} - 31{\cdot}3256.Mg^{*} - 5{\cdot}8731.Fe^{*} - 0{\cdot}1434.(Si\ Spline) - 5{\cdot}8069.Ti^{*} + 396{\cdot}622.((Fe - 0.35).Mn)^{3*} - 1{\cdot}3179.Mn^{*} - 2{\cdot}3057.B^{0.3*} + 32{\cdot}7087.Ti.B^{*} - 3{\cdot}3045$$

$$R^2 = 0{\cdot}73$$

$$Na\ spline = Na^4 - 0{\cdot}140974401.Na^3 + 0{\cdot}00663617.Na^2 - 0{\cdot}000122504.Na$$

$$Si\ Spline = Si^2 - 17{\cdot}6.Si$$

Strontium Modified Sample Set

$$\delta L(\%) = -22{\cdot}0041.Mg^{*} - 3{\cdot}9838.Fe^{*} + 0{\cdot}0555.(Si\ Spline) + 16{,}354{\cdot}8064.(Sr\ Spline)^{*} - 5{\cdot}1701.B^{0.3*} + 73{\cdot}7314.Ti.B^{*} + 1{\cdot}2911.Mn^{*} - 3{\cdot}0232.Ti^{*} + 63{\cdot}8465.((Fe - 0{\cdot}35).Mn)^{3*} + 123{\cdot}8221.Na + 20{\cdot}2351$$

$$R^2 = 0{\cdot}62$$

$$Sr\ Spline = Sr^3 - 0{\cdot}174282.Sr^2 + 0{\cdot}00898221.Sr$$

$$Si\ Spline = Si^2 - 34{\cdot}5539.Si$$

Silicon

It is difficult to appraise the effects of silicon in the above expressions as ostensibly different spline and coefficient combinations can, in fact, have very similar implications depending on the associated intercept values. For example, the silicon terms in the ductility expressions for the sodium and strontium samples do not appear compatible, yet when variation in these functions is plotted over the silicon range of interest (see Fig. 71) the two expressions are revealed as being extremely similar. This finding vindicates the full data set MLR silicon/ductility term, and thus it is the full data set silicon term which is illustrated in Figure 72. The full data set silicon/proof strength term, also shown in Figure 72 was validated in a similar manner.

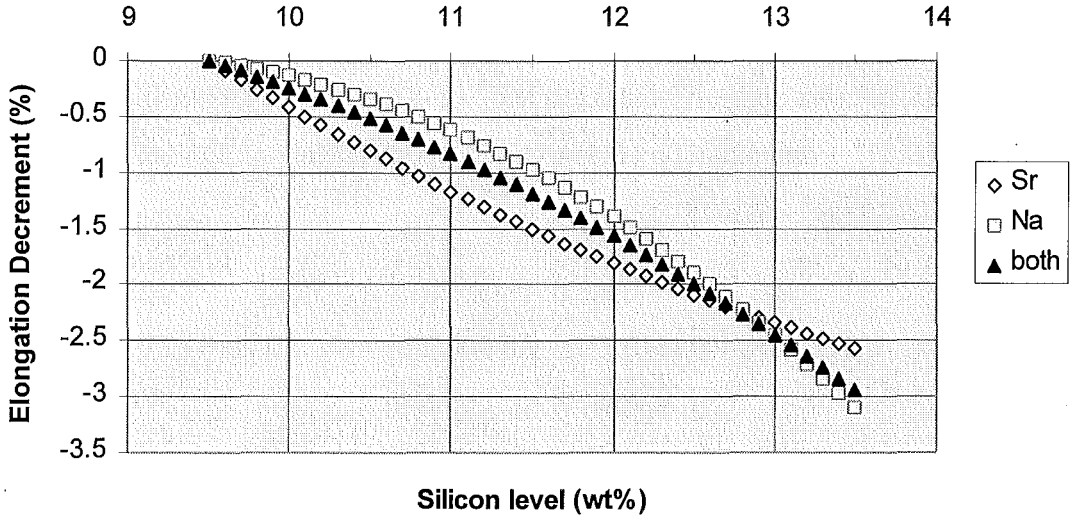


Figure 71: Comparison between the various ductility-silicon 'spline' functions given earlier.

Figure 72 also shows that proof strengths increase by up to 12 MPa as silicon levels rise from 9.5 to 12.7%. Beyond 12.7%Si this property falls only slightly (up until the analysis limit of 13.5%Si). The proof strength of Al-Si eutectic castings is seldom considered as foundry standards applicable to this alloy do not contain minimum proof strength requirements. Nevertheless, this property varies widely due to changes in composition as shown in Figure 72 and several of the following diagrams.

Figure 73 shows various MLR silicon/tensile strength terms; clearly these functions are not similar hence they are displayed on an individual basis. Whenever an element displays a variation in its effect between the sodium and strontium data sets, as in the case of these

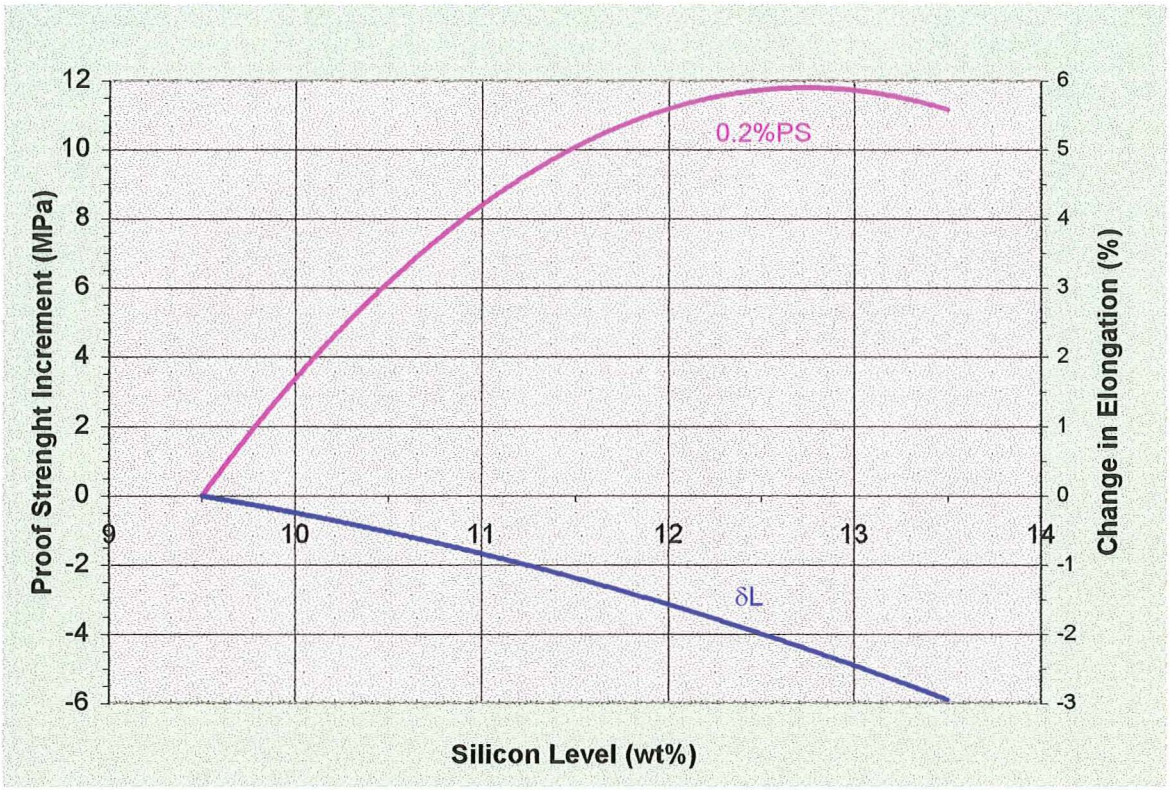


Figure 72: The effects of silicon on proof strength and ductility.

Note- These figures may not be used to find the Si component of the MLR equations.

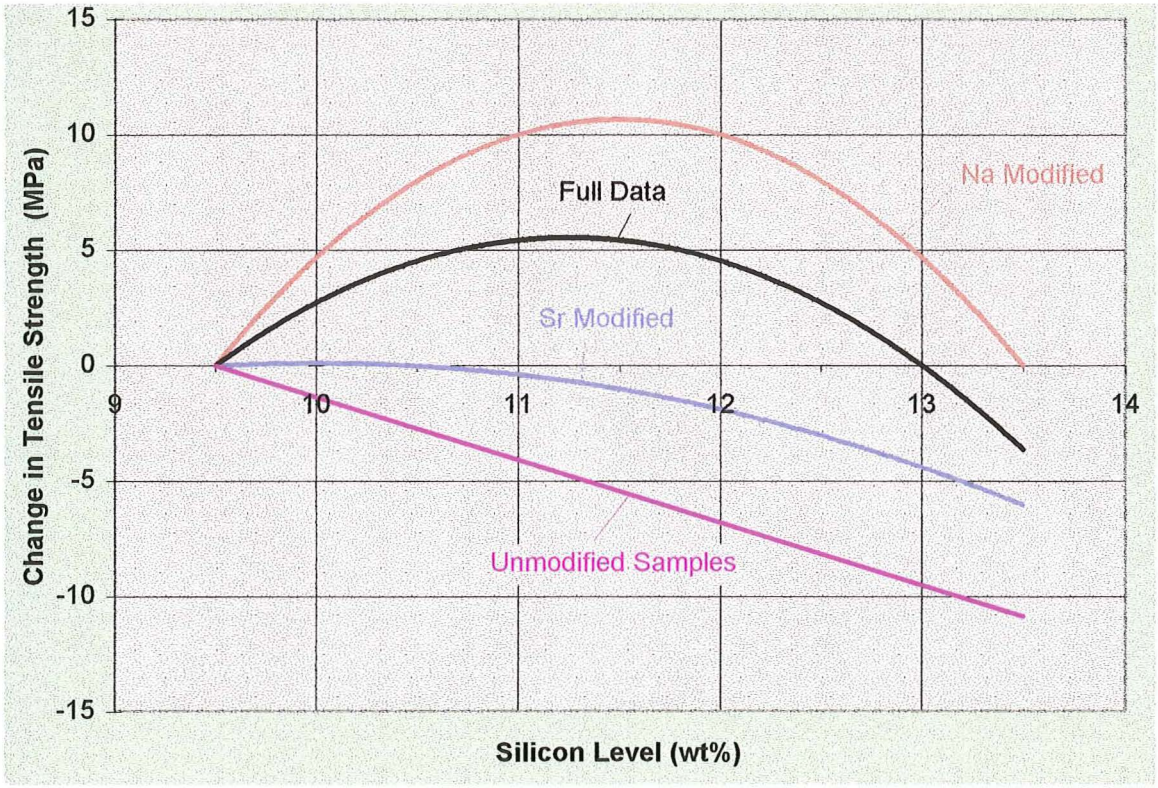


Figure 73: The effects of silicon on the Tensile strength of samples subject to various types of modification .

silicon/tensile strength functions, the implication is that modification or a modification effect interacts with the element in question. In this case, the variation in silicon behaviour suggests that a suitable modification/silicon interaction term would improve the overall MLR expression. In every case, where such interactions were indicated, efforts were made to isolate a suitable MLR interaction term; in this case none were found which displayed appreciable statistical value. The lack of an interaction term suggests that modifier effects are independent of actual modifier levels - something which seems highly unlikely.

To help reveal the interaction between modification and the effects of silicon, an MLR analysis was performed on the data stemming from totally unmodified samples. Whilst only containing 23 observations, the range of compositions in this data set encompassed each main composition variable and enabled computation of an MLR-Tensile strength expression significant to the 0.001% level. By excluding the effects and interactions of modification, the unmodified sample regression was able to quantify the effects of changing all of the composition variables of interest with acceptable statistical significance. In fact, the non-modified silicon term is an order of magnitude more significant (statistically) than the strontium-sample-set silicon term! The predictive worth (R^2) and predictive accuracy (Std Error) of the unmodified-sample-set regression were also greatly improved over those displayed by the more extensive modified-sample regression results.

Of the final MLR-derived silicon effects shown in Figure 73, the strontium and non-modified tensile strength functions are the least significant but even so, they are still significant to the 0.7% and 0.06% levels respectively. All of the remaining trends shown are significant to at least the 0.00065% level.

In the absence of sodium or strontium, increases in the silicon level from 9.5 to 13.5% progressively reduce the tensile strength by 11 MPa. When strontium is present, the tensile strength reductions are minimal below 11.5% silicon and reach a maximum of 6 MPa at 13.5% silicon. Under sodium modification increases in strength are possible, reaching a maximum of 10.5 MPa at 11.5%Si, then declining to nil at 13.5% silicon.

Sodium

Of the elements investigated, sodium has by far the greatest effect on tensile strength and ductility. Optimum strength was achieved with 0.012 to 0.018% sodium, corresponding to strength gains as high as 40 MPa (see Figure 74). Comparing the effects of sodium with those of strontium (see Figure 75), it is apparent that strontium-related strength and ductility gains are easily surpassed when using sodium, even when strontium occurs at the optimum level. Even in the sodium overmodified state tensile strength gains are higher than those possible using strontium! The gains in strength possible with sodium are of such high magnitude that correct and consistent addition of this modifier is clearly the most critical processing step in the production of castings with acceptable physical properties. Unfortunately addition of this element in a consistent manner is exceedingly difficult (see Section 2.2).

As can be seen in Figure 74, ductility variation initially follows a trend similar to that displayed by tensile strength, except that the property peak is less pronounced and occurs at slightly higher sodium levels. When sodium levels exceed 0.035%, the ductility rises once more to exceed those displayed in the initial peak; this trend continues to higher modifier levels. The increase in ductility associated with the sodium level giving optimum strength is 6%. Only in the most contaminated BS-1490-LM6 alloys (i.e. 0.6%Fe, 0.3%Mn, 0.1%Mg, 0.05%B, 0.2%Ti) is this insufficient to counteract the combined detrimental effects of iron, manganese, magnesium, boron and titanium.

There are noticeable increases in proof strength as sodium levels rise (see Figure 74). Although low statistical significance precludes accurate assessment of this proof strength effect, pronounced strength gains still occur.

It should be noted that, as mentioned above, the sodium-modified TS function displayed in Figure 74 is 13 MPa lower than that given in the listed results. This adjustment was performed to offset spline fitting inaccuracies in the 0-0.003%Na region and brings the base 9.5%Si function properties into line with those given by the strontium modified and unmodified MLR analysis results.

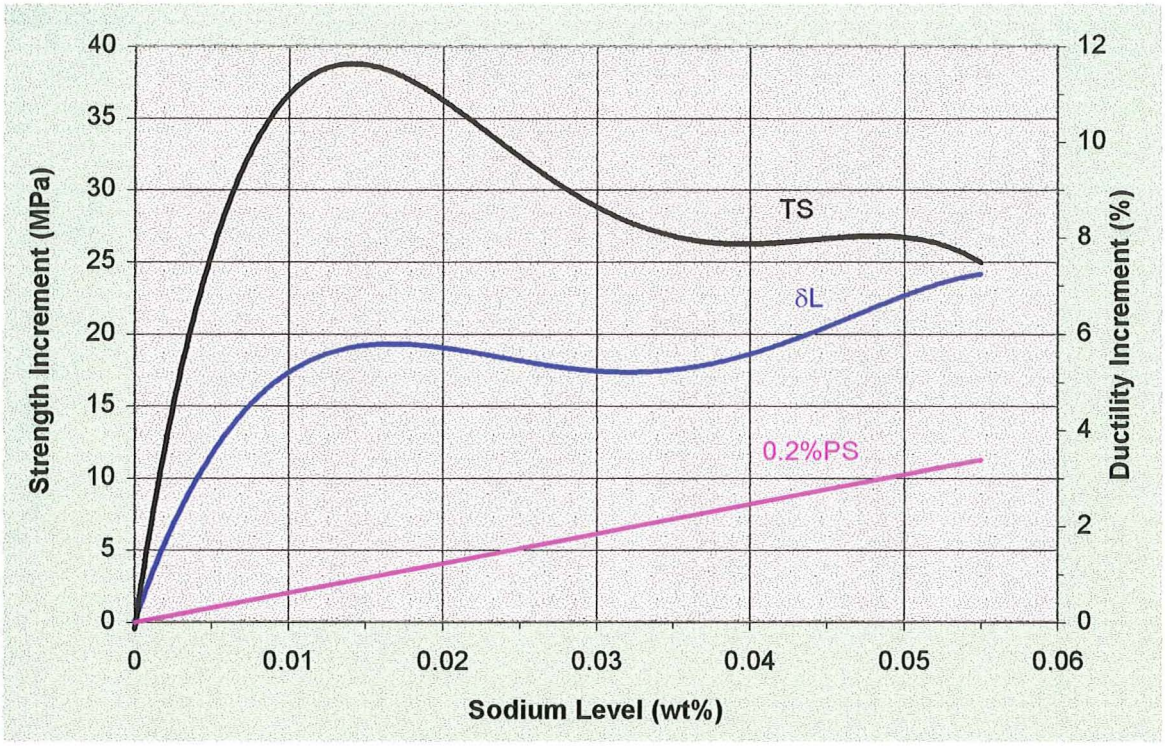


Figure 74: The effects of sodium on tensile test results.

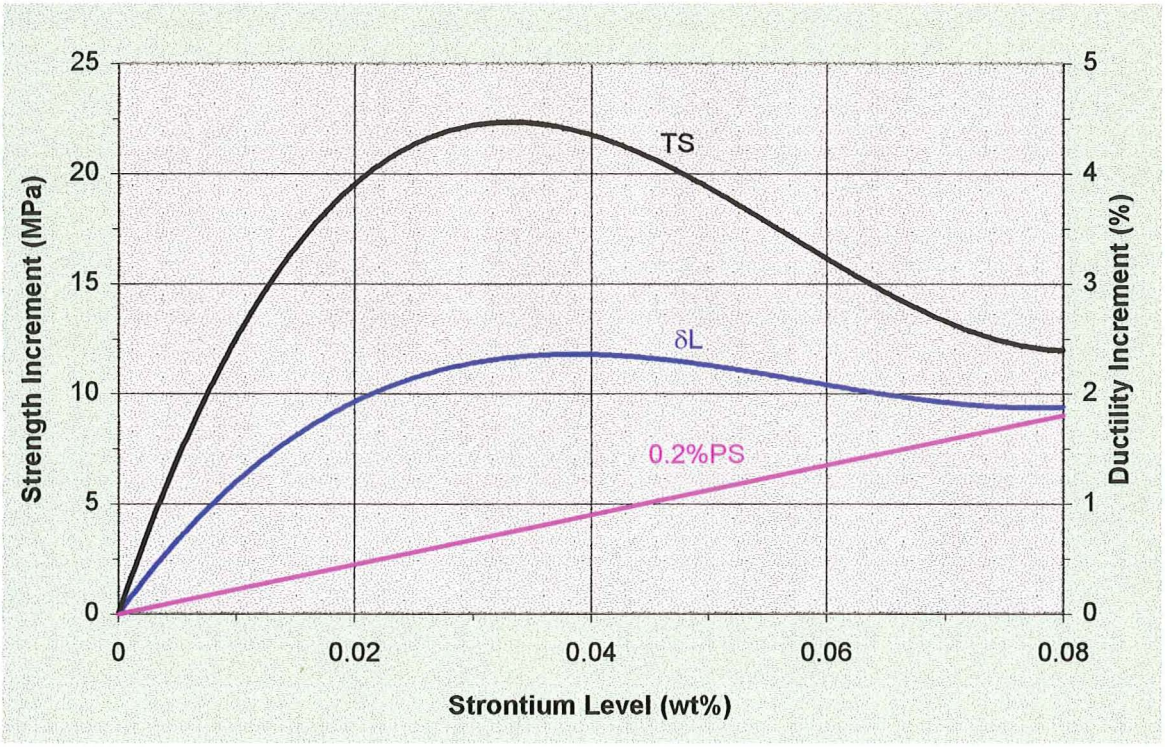


Figure 75: The effects of strontium on tensile test results.

Strontium

As mentioned above, strontium, even when added at the optimum level, does not cause the same increases in strength and ductility as are possible using sodium. The maximum gains in strength and ductility achieved with strontium modification were 22 MPa and 2.2% respectively, this corresponding to strontium contents in the range 0.02-0.045%. It is also apparent that the detrimental effects of strontium overmodification are only less severe than those encountered using sodium because the gains possible are smaller to begin with (see Figure 75). Within the strontium range investigated no indication was found that strontium overmodification gave similar ductility gains to those observed with sodium overmodification.

When processing the Al-7%Si-Mg alloy, strontium is widely accepted as being superior to sodium. This belief is based on a number of issues, the more significant being: the effects of overmodification are not as severe with strontium; strontium is easily added to foundry ingot prior to purchase and no subsequent additions need be made; the Al-7%Si-Mg alloy is widely used for permanent-mould casting (a situation where differences between sodium and strontium modification are small) and finally, the problems associated with increased gas levels following strontium addition have largely been overcome. The results given by the Al-Si eutectic alloy clearly suggest that for this alloy, any handling benefits strontium may afford are insignificant in comparison to the strength gains possible using sodium.

As was the case with sodium addition, proof strength increased noticeably as strontium levels rose and similarly it was not possible to quantify this effect with any real accuracy.

Iron

As shown in Figures 76 through 79, the effects of iron are closely interrelated with the effects of manganese. This is exactly what was expected since, as mentioned in Chapter 2, manganese is often added deliberately to form $(FeMn)_3Si_2Al_{15}$ thus combining the iron into a supposedly less detrimental phase than $FeSiAl_5$. Both the iron and iron/manganese phases were observed within the cast specimens and are shown in Plates 22 and 23.

When the strengthening effects of iron alone are analysed it becomes obvious that the effects of iron are strongly related to the modification state (see Figure 80). When iron occurs in an unmodified structure it produces significant reductions in strength. Conversely, in structures modified with either sodium or strontium, significant strength

increases occur. The various MLR ductility results indicate that introducing 0.5% iron reduces ductility values by approximately 25% of their value, irrespective of the initial ductility level. Unfortunately, the MLR ductility results for the unmodified sample set did not show high statistical significance. Accordingly, these results are contained in Appendix O but are not listed above.

The implication from these results is that increased iron levels in already brittle, unmodified structures results in decreased strength due to the severe ductility limitations. In more ductile, modified structures the embrittling effect of iron is more pronounced, but due to the higher inherent matrix ductility, strength is no longer dominated by the effects of the embrittling impurity phases. Prior to failure, iron acts as a conventional second phase hardener. Consequently, in structures not dominated by ductility limitations the iron acts as a strength enhancer. While no iron/modifier interaction terms were established, it is obvious that the embrittling effects of iron may be offset by minor modifier additions. It is therefore conceivable that the strength of castings containing very low modifier levels may also have been compromised by ductility limitations. This effect would be more pronounced in samples containing the weaker strontium modifier thus supporting the finding that, on average, iron phase strengthening is less pronounced in strontium modified samples than those containing sodium.

No interaction between iron and the modifiers or iron and manganese was indicated by the proof strength results. As shown in Figure 81, iron has a strong beneficial effect on proof strength with the magnitude of this effect being independent of the modifier used. Compared to virgin alloy containing 0.1-0.2% iron alloys containing 0.6% iron display increases in proof strength of up to 10MPa (≈14%).

Figures 76 through 79 show the significance of the Fe/Mn interaction and how the effects of the Fe/Mn combination depend on the modifier used. With sodium modification, property variations are relatively uniform until combined iron and manganese levels exceed 0.75%. Above this value, strength rapidly decreases while ductility gradually improves. Within the range 0.1-0.7% Fe and 0-0.55% Mn, total strength losses due to high combined iron and manganese levels, exceed the potential gains due to iron alone, resulting in reductions as high as 16 MPa and overall strengths 4-5 MPa lower than indicated by virgin alloy (0.1-0.2% Fe). Improved ductility due to manganese addition beyond the Fe + Mn

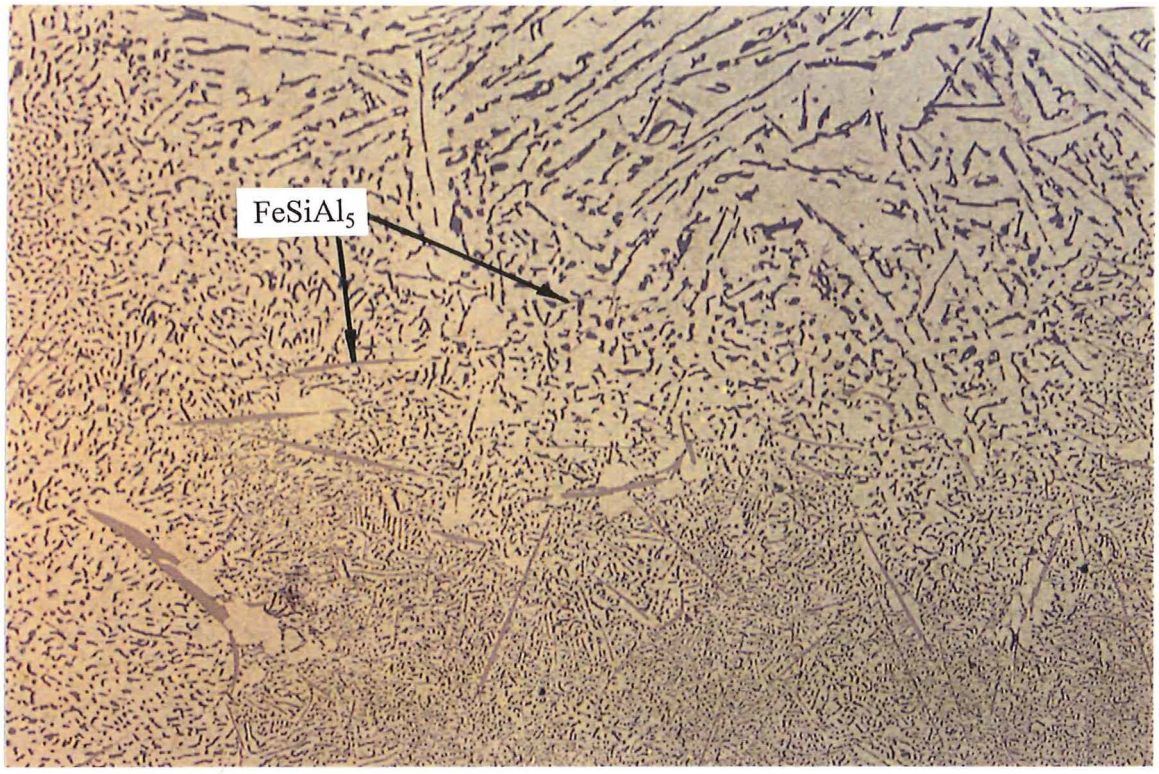


Plate 22: $FeSiAl_5$ needles as observed in the microstructure of sample 118-1-25 (x220).

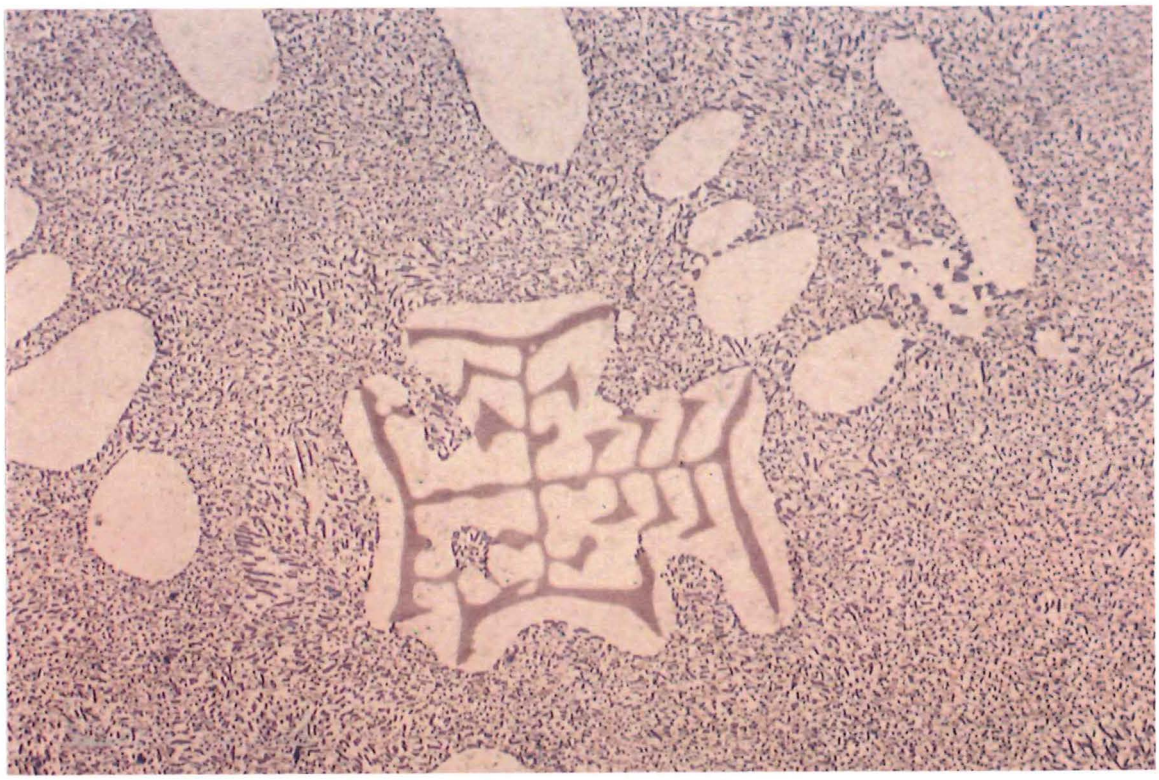


Plate 23: $(FeMn)_3Si_2Al_{15}$ script as observed in the microstructure of sample 78-3-42 (x110).

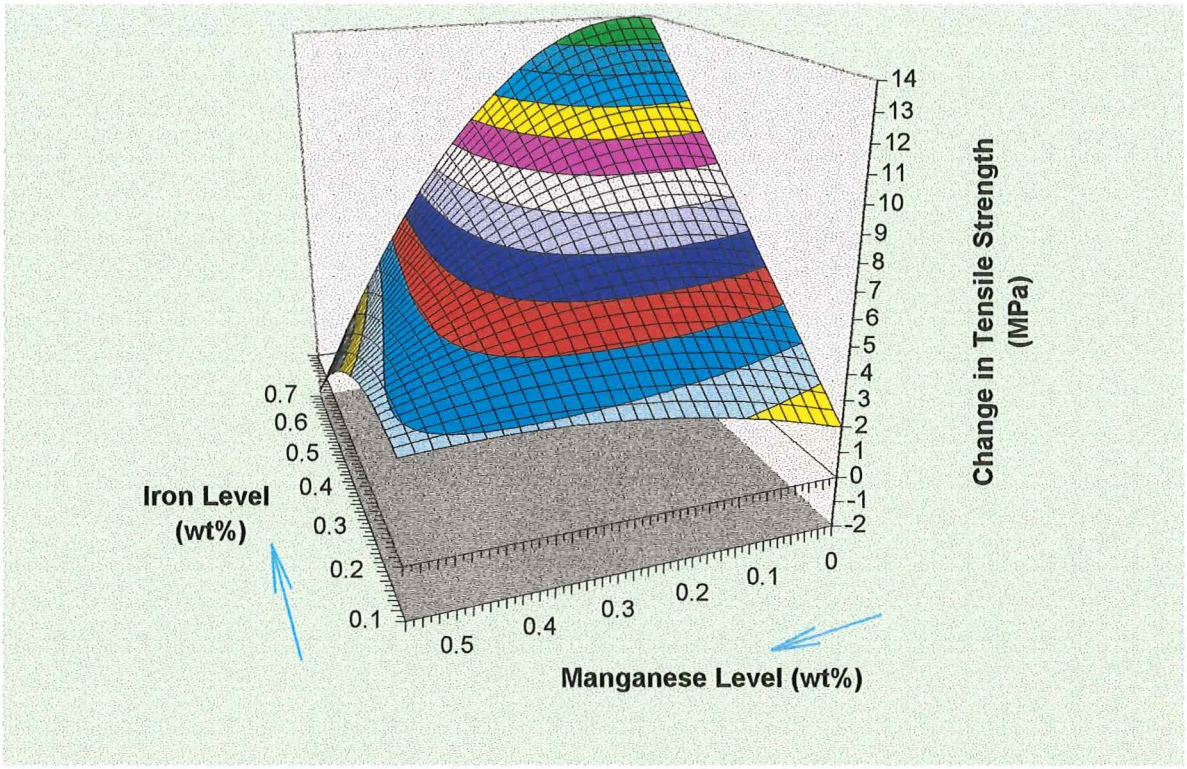


Figure 76: The iron-manganese tensile strength interaction in sodium modified castings.

Note- An extrapolation to 0%Fe is required to obtain the origins of these two charts.

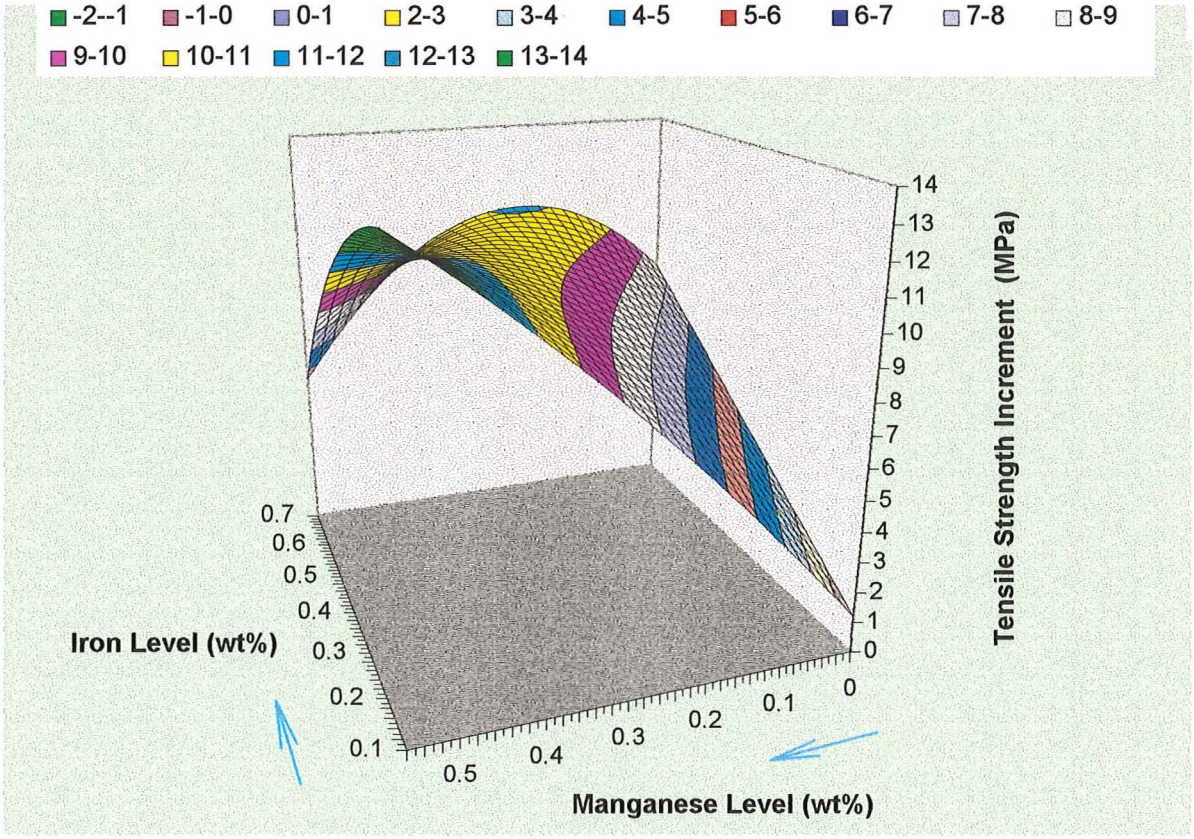


Figure 77: The iron-manganese tensile strength interaction in strontium modified castings.

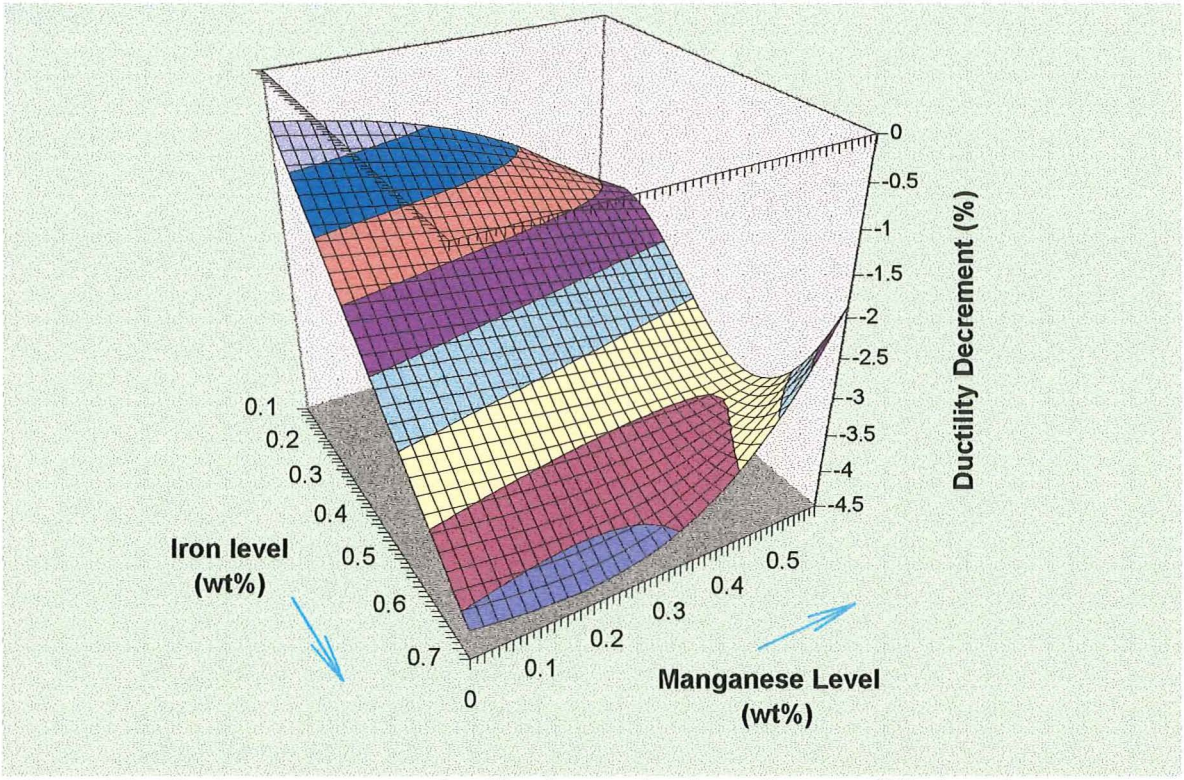


Figure 78: The iron-manganese ductility interaction in sodium modified castings.

Note- An extrapolation to 0%Fe is required to obtain the origins of these two charts.

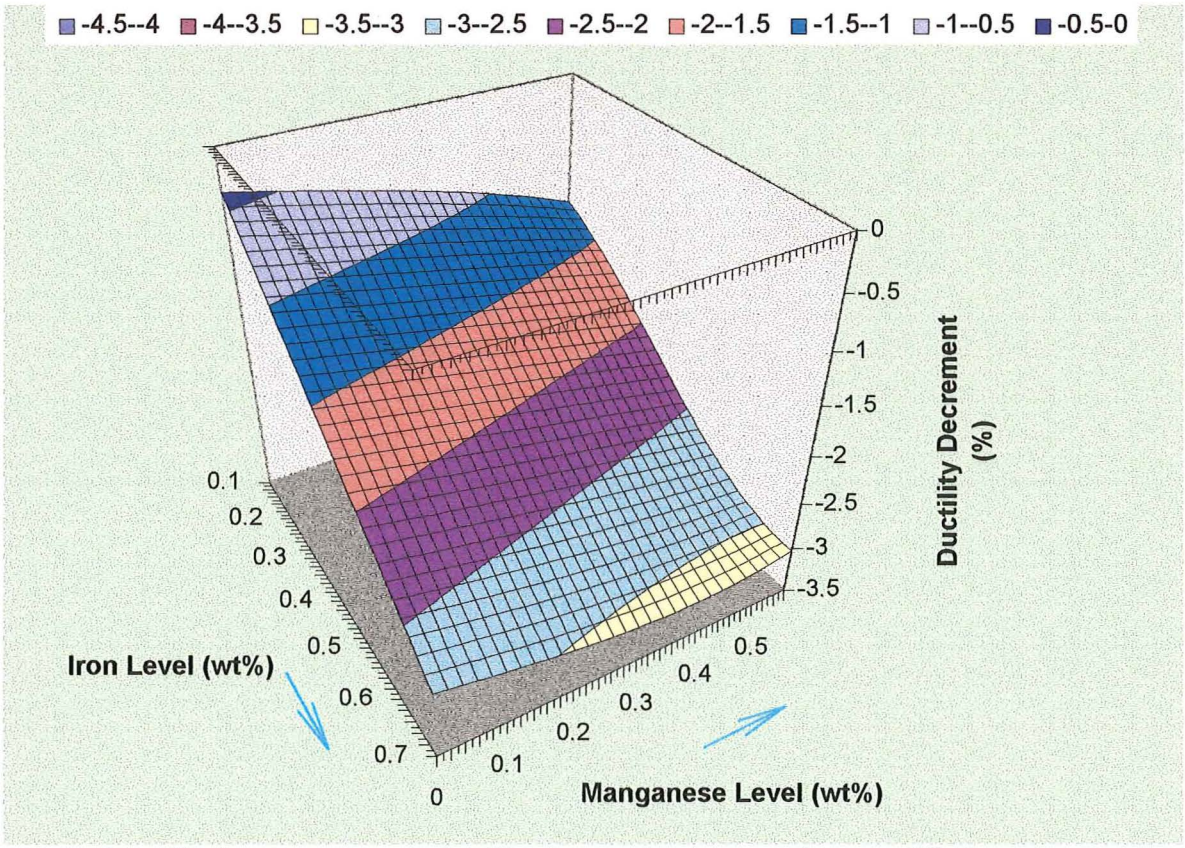


Figure 79: The iron-manganese ductility interaction in strontium modified castings.

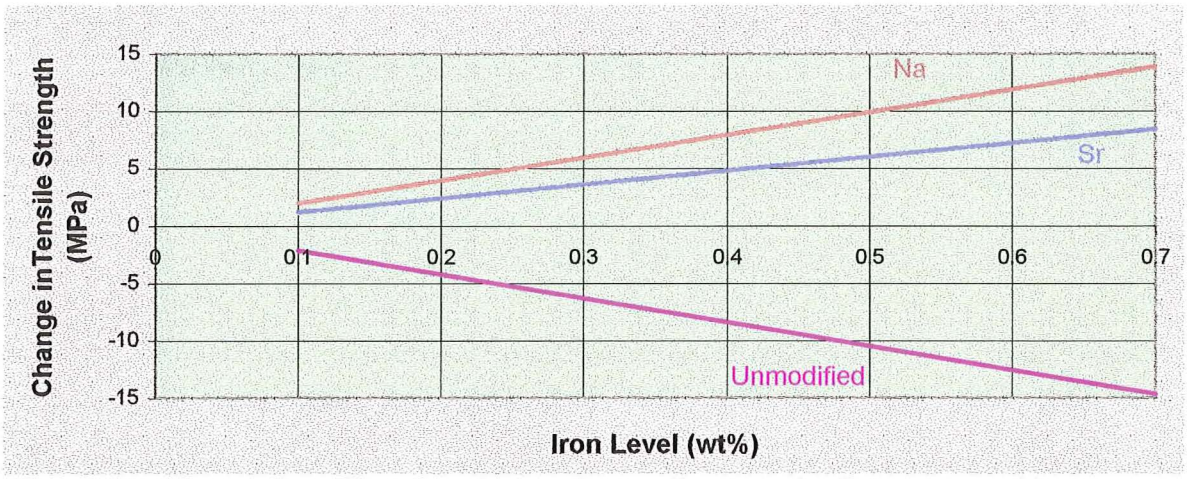


Figure 80: The varying effects iron has on the tensile strength of structures subject to differing modification techniques.

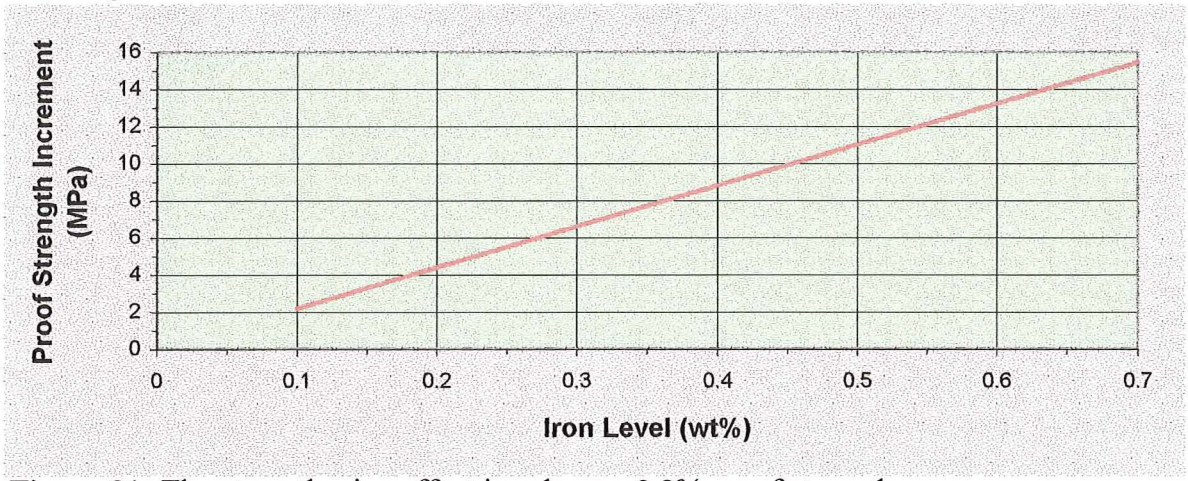


Figure 81: The strengthening effect iron has on 0.2% proof strength.

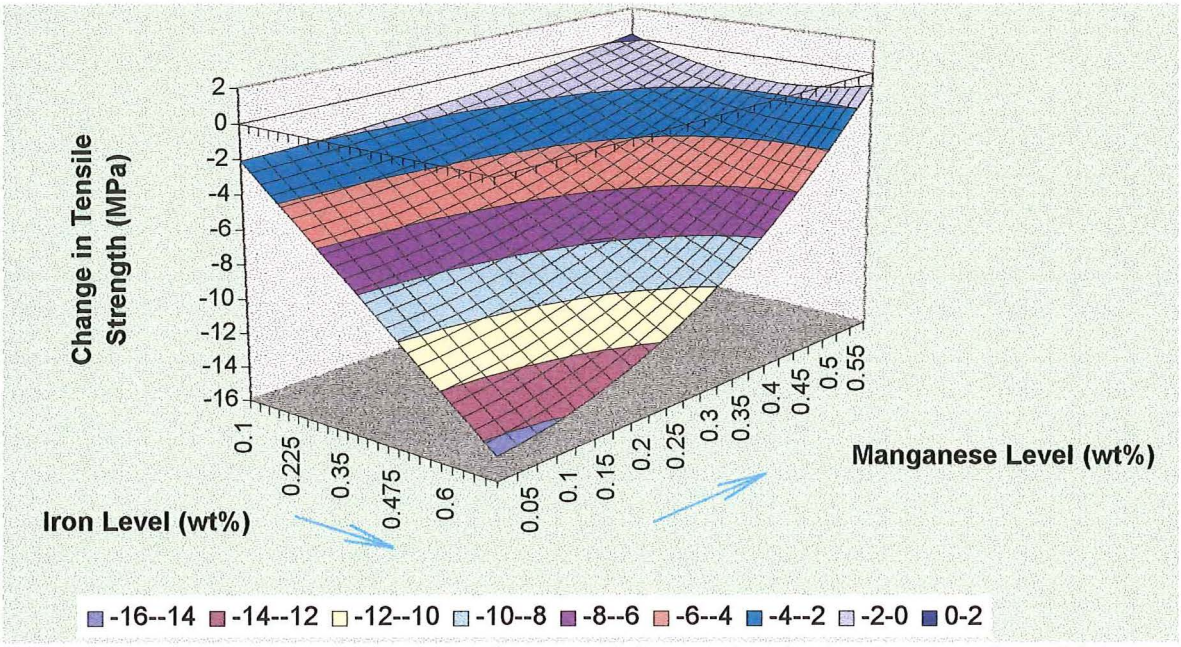


Figure 82: The iron-manganese tensile strength interaction in the absence of modifying elements.

= 0.75% level, produces elongation at fracture values up to 2.5 units higher than would otherwise be expected. Whatever causes ductility to improve in this region does so at the expense of strength, not only eliminating gains due to iron strengthening but acting in itself as a weakening agent.

Strontium modification results in the tensile strength effects of manganese being much more beneficial and pronounced than that encountered in unmodified and sodium modified samples. Excepting this difference, similarities can be seen between the two modified tensile strength Fe/Mn surface plots. As with sodium, strontium modification combined with high iron and manganese levels also results in rapid strength decreases. The onset of this effect occurs at slightly higher impurity levels with strontium modification with strength decreases not being significant until combined iron and manganese levels exceed 0.85%. Using strontium modification with high iron and manganese levels of 0.7 and 0.55% respectively, maximum strength is severely compromised, dropping some 8-10 MPa. These losses are not sufficient to completely eliminate the strength gains due to iron alone. In contrast to sodium modified samples, the rapid strength losses encountered at high iron and manganese levels are not accompanied by reductions in the detrimental effects iron has on ductility. In the strontium modified case no increase in either strength or ductility result from iron and manganese levels exceeding 0.85%.

Since no highly significant manganese factors could be found in an MLR analysis of the unmodified sample ductility data, only the strength effects of the Fe/Mn interaction can be assessed in the absence of a modifier. While the results shown in Figure 82 indicate that 0.5% Mn is sufficient to counteract the effects of iron irrespective of the iron level, this can not be fully confirmed due to the limited number of observations on which this diagram is based. It can be concluded that manganese additions increase the strength of high-iron unmodified alloys. Since ductility is the dominant factor controlling the strength of unmodified alloys it is very likely that manganese additions also improve the ductility of high-iron unmodified alloys.

Manganese

As discussed above, the effects of manganese and iron are closely interrelated.

When the effects of manganese alone are investigated it is apparent that ductility effects are independent of the modifier used, while strength effects are not (see Figures 76-79). As manganese levels rise from zero to 0.5% the recorded extension after failure values drop by $\approx$ 1.5 units. This increasing embrittlement occurs at a relatively uniform rate as manganese levels rise. The strengthening effects of manganese are the same for sodium modified and unmodified specimens, in each case manganese levels rising from zero to 0.5% result in strength increases of 2-3 MPa. When strontium modification is employed manganese strengthening is far more conspicuous, increasing in magnitude by a factor of approximately five. Manganese strengthening by as much as 13 MPa is cumulative with the effects of iron, until the combined iron and manganese levels exceed approximately 0.85%.

No explanation has been found as to why manganese additions produce differing effects depending on the modifier used. It is possible that either the solidification of the manganese phase is directly influenced by the modifying elements, or the modification-induced eutectic shift and resulting dendrite proportions, change the size of the manganese phase and hence its effects. The latter is extremely unlikely, as the eutectic shift is strongly influenced by both modifiers, with sodium acting little differently to strontium. To investigate the former possibility, the manganese phase present within several unmodified, strontium-modified and sodium-modified samples were micrographically compared. Little difference could be seen between the two modified structures with the "Chinese script" $(FeMn)_3Si_2Al_{15}$ occupying whole regions of individual dendrites. In unmodified samples the script phase was noticeably smaller, typically not spanning entire dendrite widths as was prevalent in the modified cases. The results of this brief study have not resolved the question of why manganese effects differ depending on the modifier used, however a more extensive microstructural analysis may well shed more light on the issue.

The effect of manganese on proof strength was not significant in the unmodified and sodium modified samples. It did however, cause very minor strength gains in the strontium modified samples. The minor effect (3-4 MPa with a 0.5% Mn gain) on the strontium samples has not been illustrated as it was not associated with high statistical significance (P value 16%).

Magnesium

As shown in Figures 83 through 85, magnesium has detrimental effects on both the tensile strength and ductility of modified structures. The decrease in tensile strength is closely related to the level of eutectic refinement with the largest strength losses associated with optimum refinement. Since sodium produced finer eutectic structures than strontium, samples modified with the former were affected by magnesium to a greater extent. These findings are in agreement with the modification MLR results given in Section 8.2.1, which show that magnesium acts to reduce modification levels and hence increase the modifier levels required to achieve optimum eutectic refinement. If increased modifier levels are capable of counteracting magnesium, strength *increases* should be observed in samples containing high levels of magnesium and what would otherwise be slightly excessive modifier. Functions incorporating strength gains in the regions 0.015-0.03Na and 0.03-0.045Sr were tried in the MLR strength expressions, however all were found to be inappropriate. The result of this finding is that magnesium coarsens the eutectic structure however, maximum strength still occurs at modifier levels equivalent to optimum refinement in magnesium-free structures. A possible explanation of why magnesium induced strength losses are not eliminated by higher modifier levels, is that modification may become less uniform as magnesium levels rise. Micrographic analysis revealed that samples containing high levels of magnesium display distinct banding (see Plate 24) with the $(FeMg)_3Si_6Al_8$ phase associated with the undermodification bands. Samples containing magnesium and excessive modifier levels displayed both over- and under-modified bands within the same microscopic region leading to final modification ratings which could be misinterpreted as indicative of optimum eutectic refinement. The eutectic regions surrounding the various under-modification bands displayed modification levels much as would be expected given the modifier level alone. This observation supports the finding that magnesium-compensation, via the addition of increased modifier, is not appropriate for the elimination of detrimental magnesium effects.

If the above trends persist at lower silicon and higher magnesium levels sand-cast unheat-treated Al-7%Si-Mg alloy should show optimal strength at a modification ratings slightly lower than that expected.

The statistically significant modifier-magnesium functions used in the MLR modified sample sets indicate that magnesium has no influence on the tensile strength of unmodified

structures; the statistically significant results of regressing the unmodified sample data alone shows this to be incorrect. As illustrated in Figure 86, magnesium is beneficial to the strength of unmodified structures. This indicates that the magnesium phase acts as a strengthener and has minimal detrimental effect on the eutectic coarseness of unmodified structures. This is supported by the microstructures of unmodified magnesium-containing samples displaying no discernible silicon coarsening in the regions adjacent to magnesium precipitates. It would thus seem that magnesium interacts with the modification process rather than the silicon directly.

In unmodified structures, the strengthening ability of the magnesium phase is evident. In modified structures this effect is outweighed by detrimental interactions with silicon refinement.

As could be expected from the above results, magnesium is also detrimental to ductility with the embrittlement more pronounced in the sodium than strontium samples. Interestingly, the detrimental effects that magnesium has on ductility are potentially as bad as those caused by iron. For example, a 0.6% increase in iron reduces ductility by approximately 3.5 units whereas, a similar embrittlement is caused by a 0.1% increase in magnesium.

Irrespective of the modifier used, proof strength consistently increases as magnesium levels rise (see Figure 85). This effect was associated with substantial variability, making it difficult to detect in the strontium modified sample set.

Titanium

As shown in Figures 87 through 89, titanium is beneficial to tensile strength but slightly detrimental to ductility. Titanium was shown to interact with boron in the ductility MLR, yet no interaction terms could be found for either tensile or proof strength expressions. In the case of proof strength, titanium did not have an influence large enough to be determined with appreciable statistical significance.

While no statistically significant complex titanium or titanium/modifier strength functions could be found, it is clear from Figure 87 that titanium imparts greater strength improvements to structures which contain, on average, coarser silicon. From the regression results it can be seen that a 0.2% titanium addition causes strength gains of 8 MPa in unmodified structures, while similar additions to the sodium modified samples

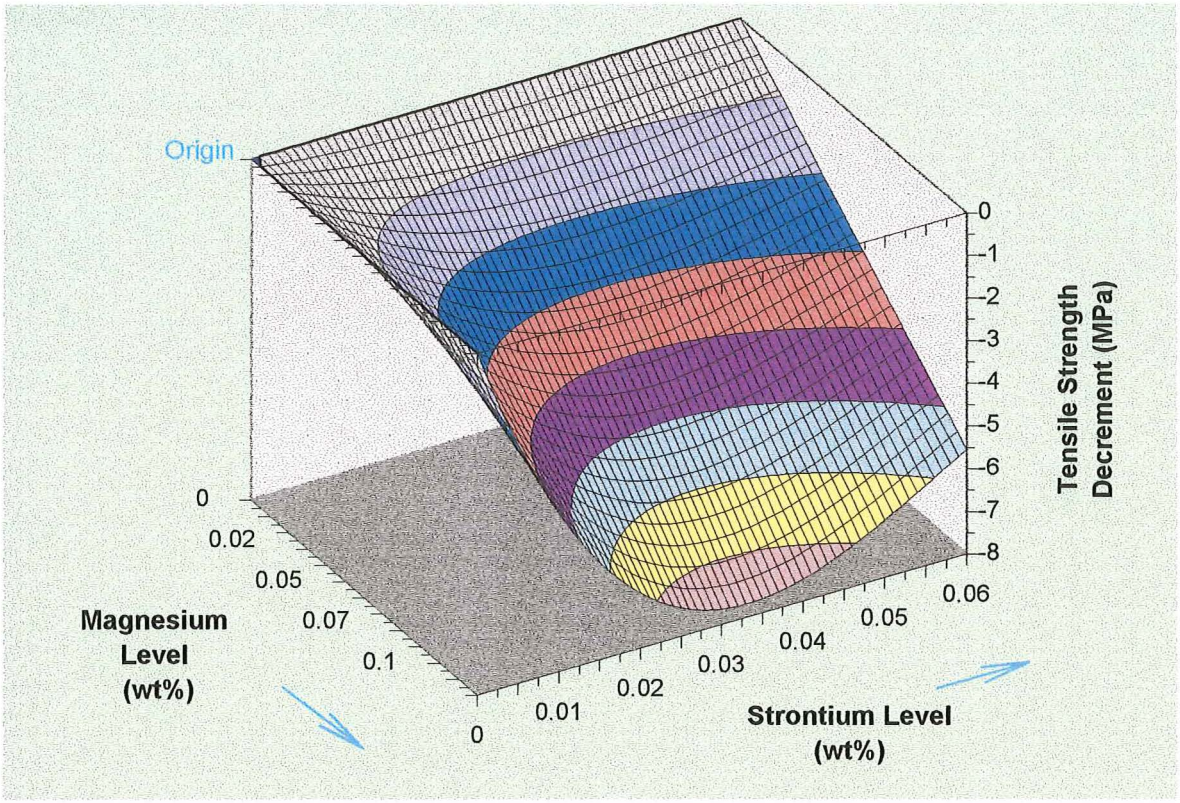


Figure 83: The weakening effect of magnesium in strontium modified alloy.

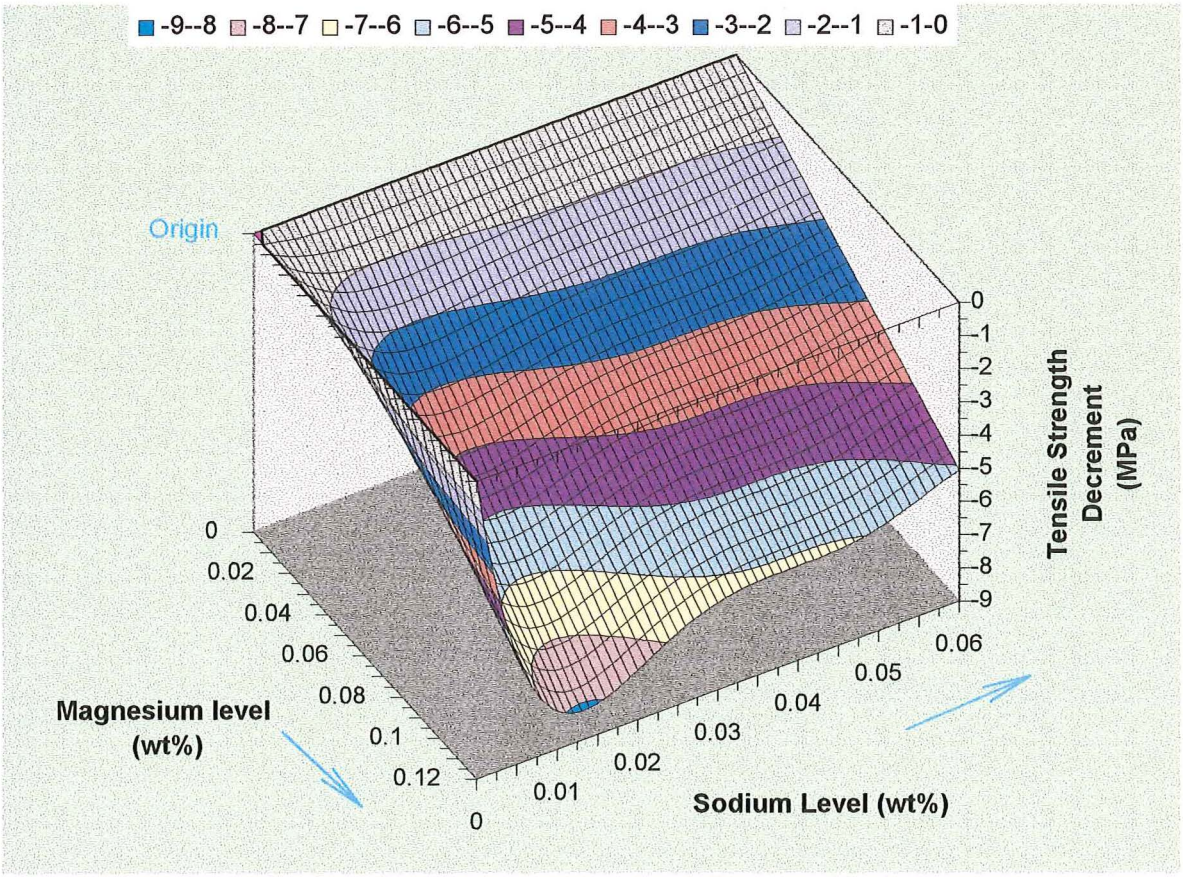


Figure 84: The weakening effect of magnesium in sodium modified alloy.

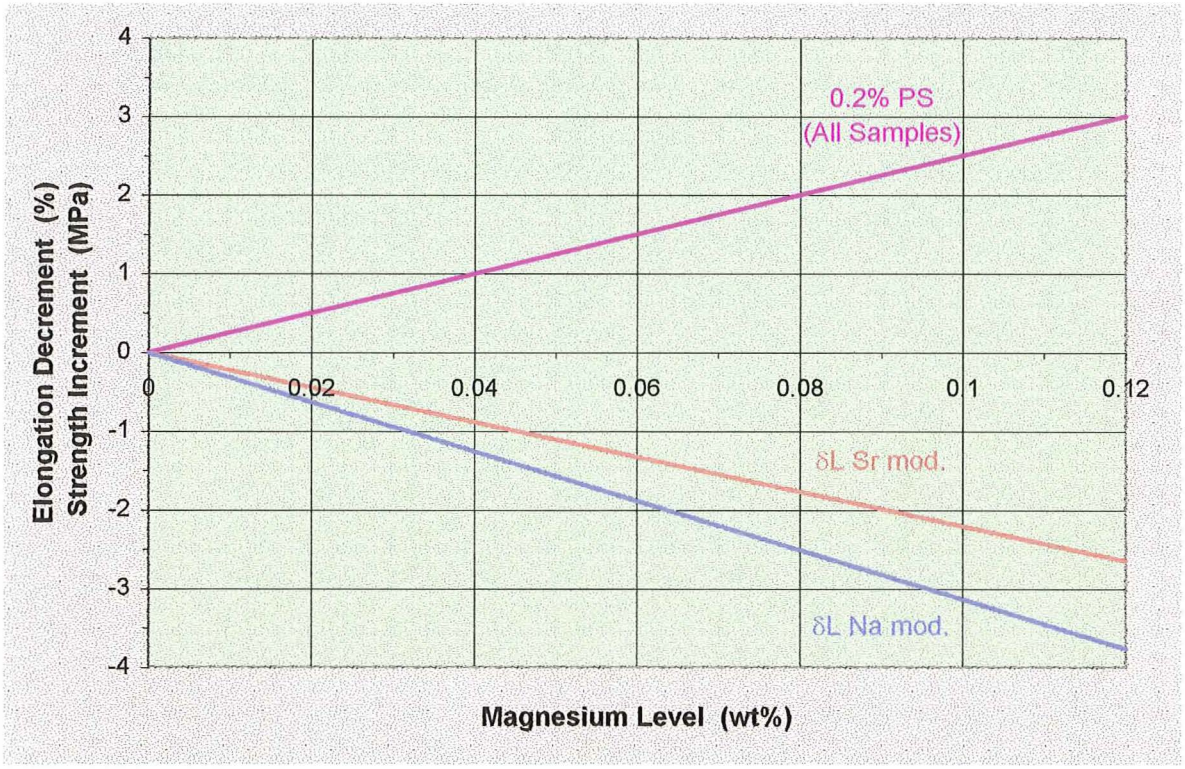


Figure 85: The effect of magnesium on the 0.2% proof strength and ductility of sand-cast Al-Si eutectic alloy.

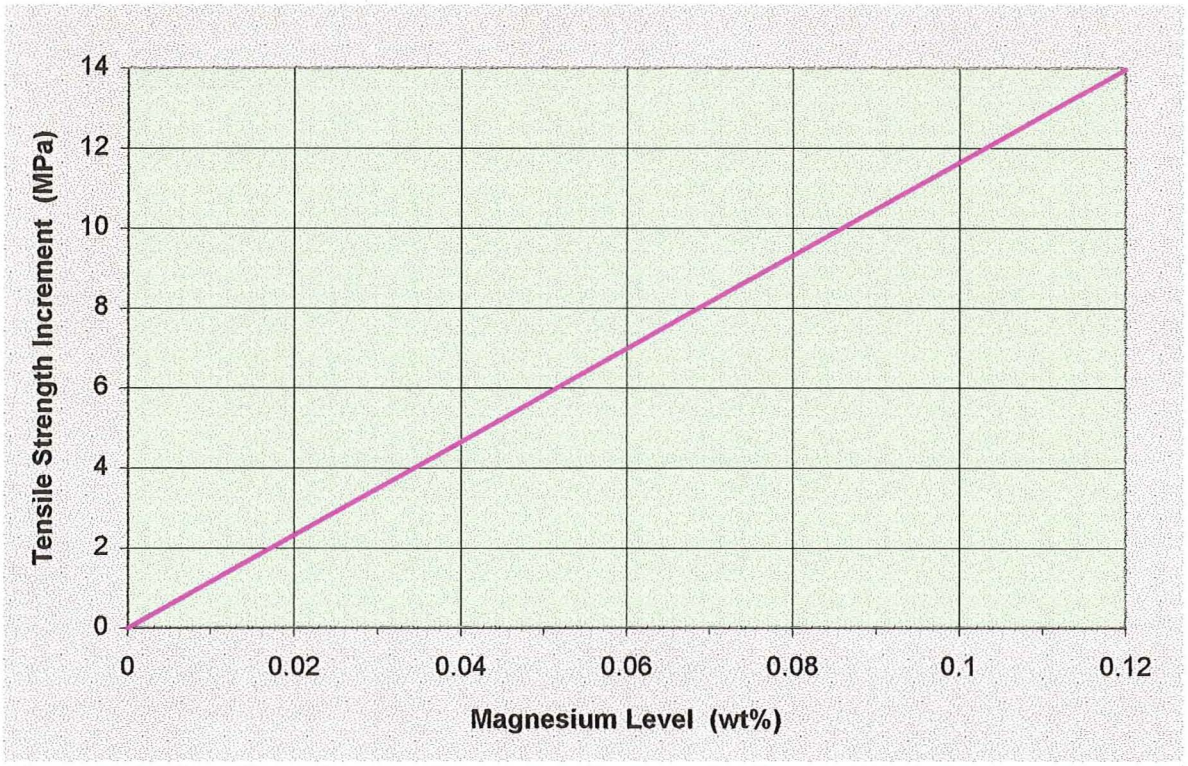


Figure 86: The effect of magnesium on tensile strength of unmodified alloy.

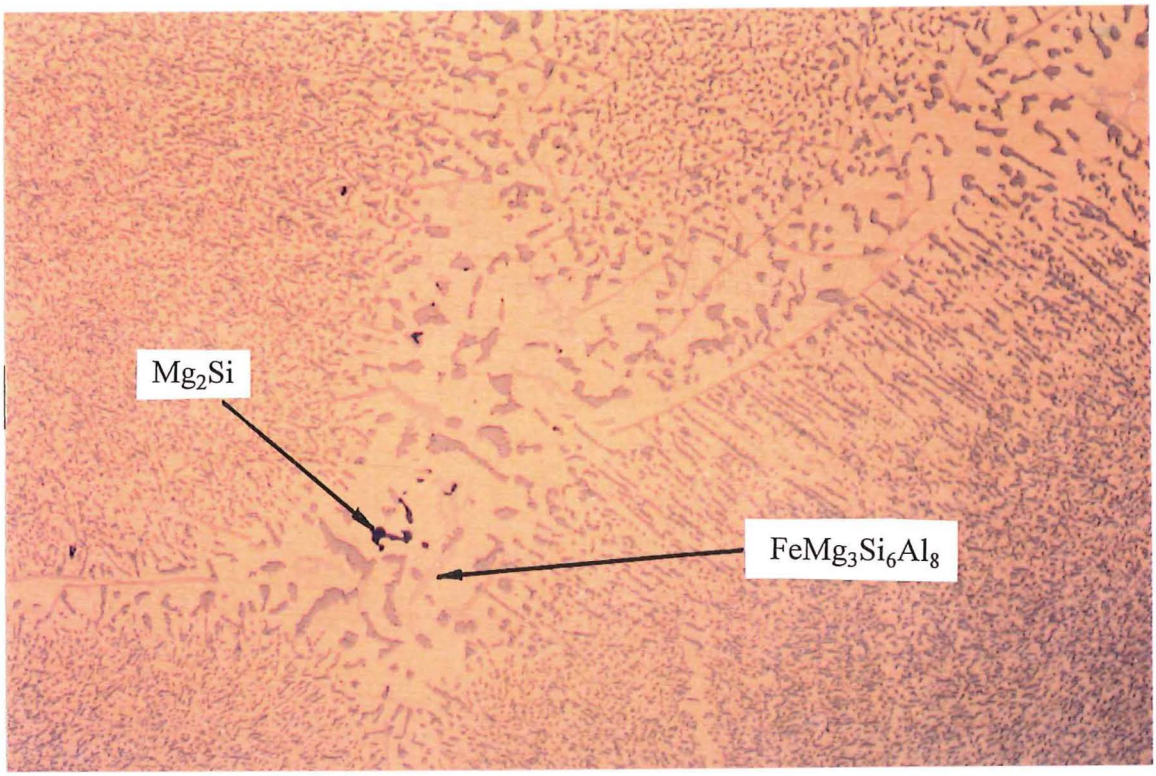


Plate 24: Magnesium induced modification banding as observed in the microstructure of sample 79-1-26 (x228).

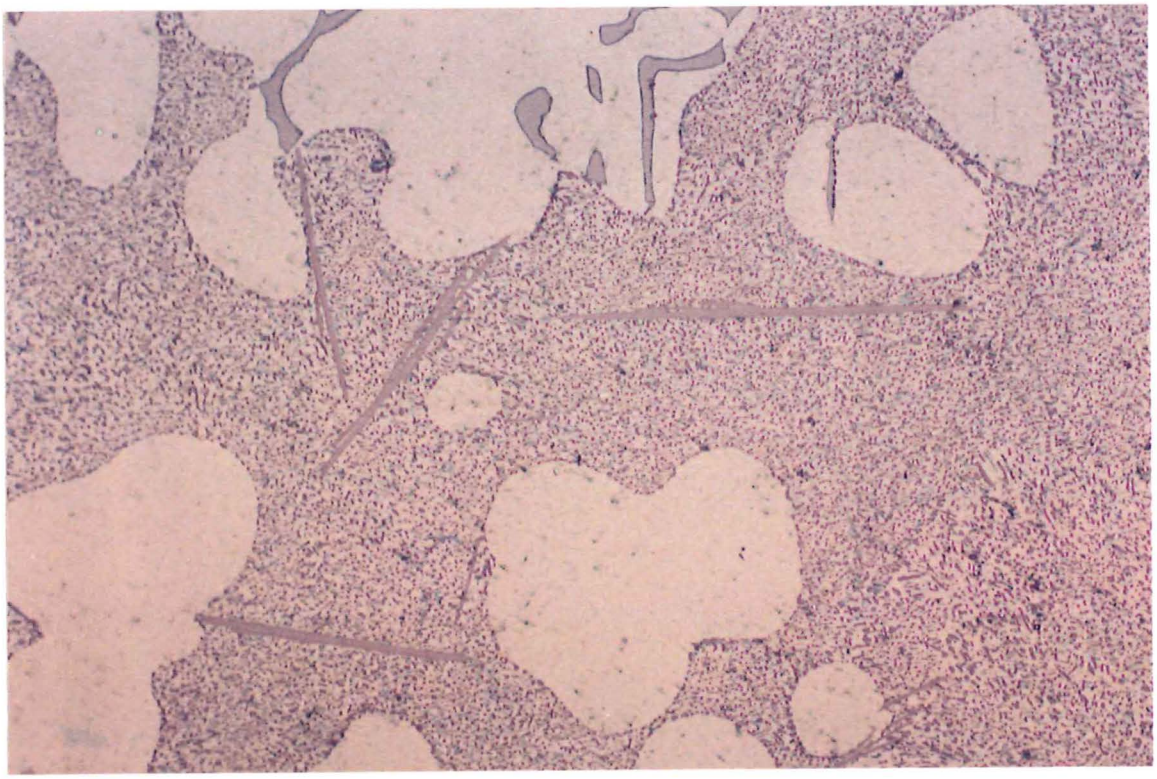


Plate 25: TiAlSi needles as observed in the microstructure of sample 29-3-79 (x220).

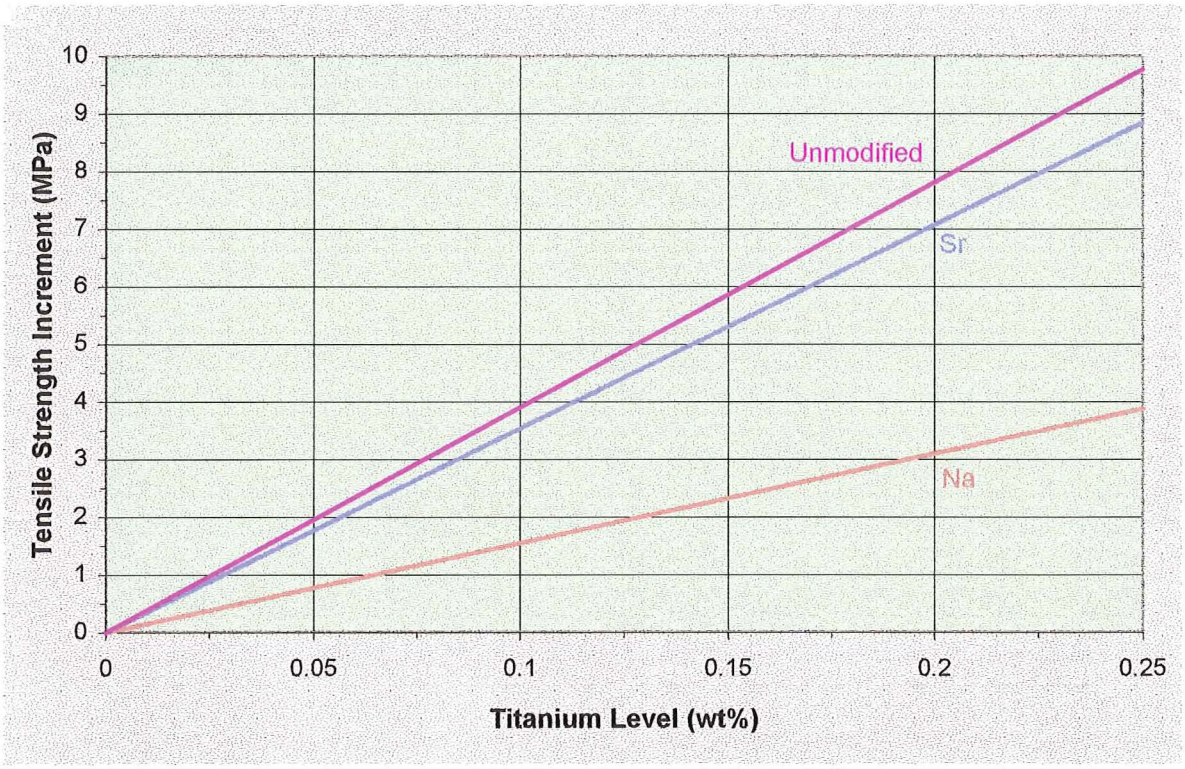


Figure 87: Titanium-induced strengthening characteristicis of alloys exposed to various modifiers.

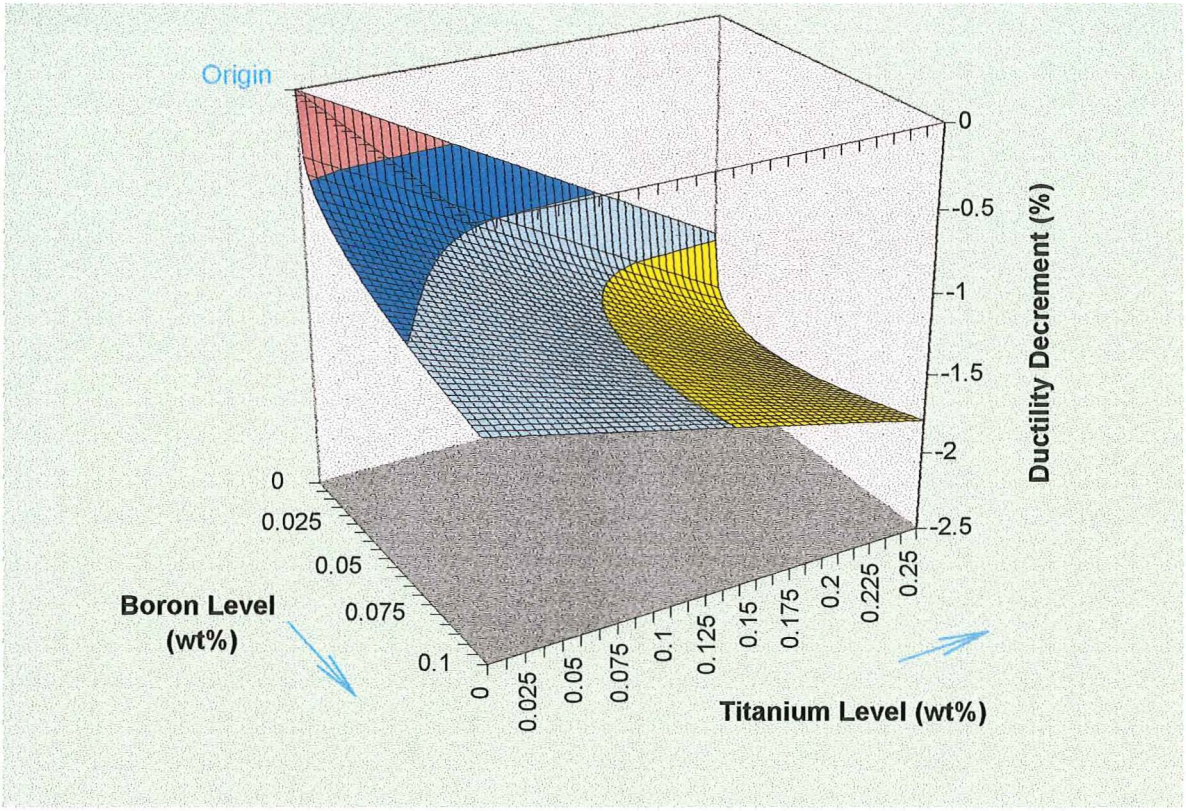


Figure 88: The titanium-boron ductility interaction displayed by sodium modified samples.

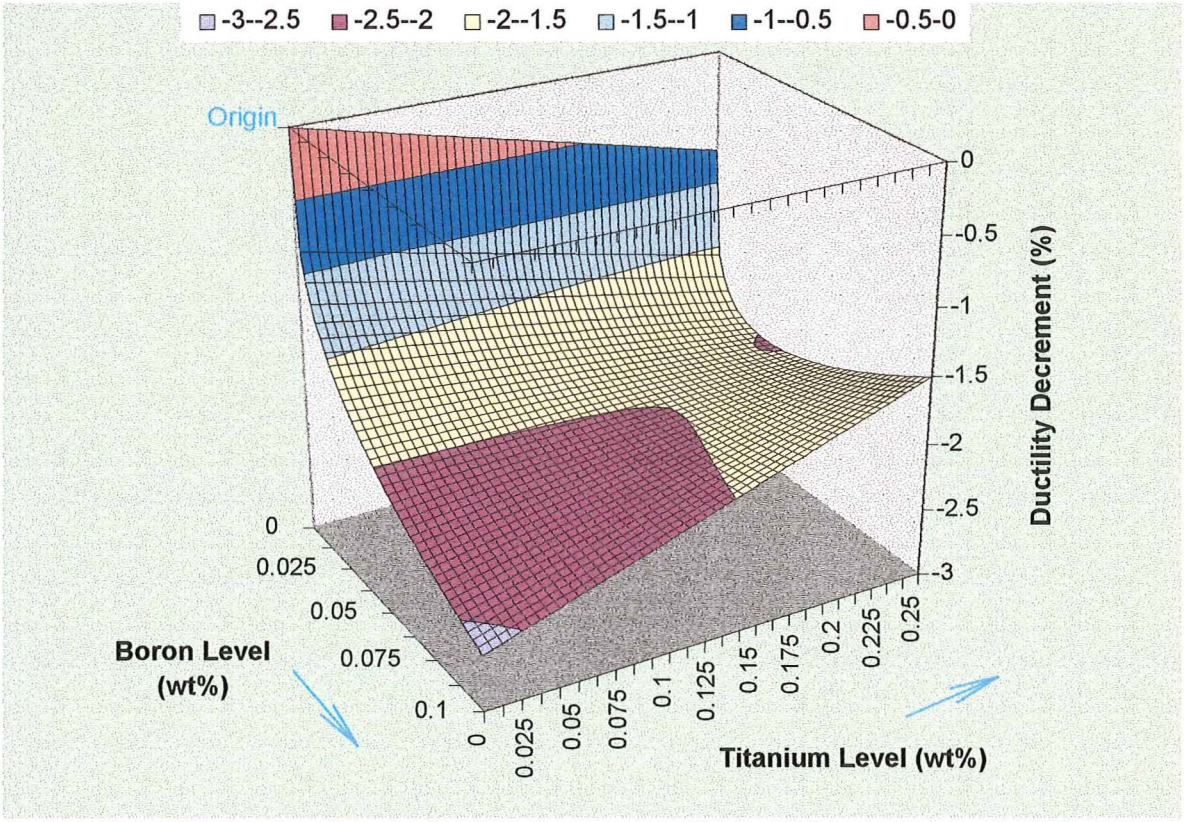


Figure 89: The titanium-boron ductility interaction displayed by strontium modified samples.

produced gains of only 3 MPa. Given that it was established earlier that titanium acts as a eutectic silicon refiner, the fact that titanium tensile effects are related to modification is not surprising.

Micrographic analysis of several modified and unmodified samples revealed that modification was extremely uniform throughout the titanium-containing castings. Unmodified samples containing titanium also displayed regular and noticeable silicon refinement. In samples containing more than ≈ 0.12%Ti, TiAlSi needles were observed (see Plate 25). No discontinuities were observed in refinement of eutectic regions adjacent to these precipitates. The above observations suggest that dissolved titanium promotes eutectic silicon refinement and the process by which it is achieved is both compatible with and complementary to conventional modification.

The ductility functions, displayed in Figures 88 and 89, show the interaction of titanium and boron and the detrimental effects each of these elements has on ductility. The results of the sodium sample MLR suggest that within the limits of 0.2% titanium and 0.1% boron, each of these elements has detrimental effects similar in magnitude, i.e. elongation's decrease by ≈ 1.2 units each. When these elements occur in combination the detrimental effects of each are not fully compounded as the level of compounding decreases as the combined levels rise. The boron and TiB interaction terms in the sodium modified sample results were not found with high statistical significance (p-values 4.8% and 17.6% respectively). Since the calculated 95% certainty regions display very small overlap with the equivalent regions from the strontium sample results, it is unlikely that the effects are similar in cause between the two modification groups.

The trends evident in the strontium-sample results are similar to those given by the samples modified with sodium, however, the effects of titanium are reduced by nearly 50%, while those due to boron more than double as does the interaction term. The large positive influence of the interaction term suggests that when boron levels exceed ≈ 0.04%, any titanium additions moderate embrittlement so improving both strength and ductility. No similar situation exists for boron as even minor additions in the presence of either modifier result in substantial embrittlement.

Boron

Irrespective of the modifier used, boron is detrimental to all three measured tensile properties. Figure 90 illustrates the tensile and proof strength effects of boron addition. No statistically significant boron/proof strength term could be found in the sodium modified results and hence none is displayed. The large loss of tensile strength (10-14 MPa with 0.1% addition) caused by boron additions must be put in perspective as BS1490-LM6 limits boron levels to half (and commercial additions seldom reach even a quarter) of the maximum level displayed in Figure 90, i.e. 0.05%. Since most of the effects that boron has on ductility occur at very low addition levels, the above comments regarding strength do not apply equally to elongations at fracture.

What is clear from Figures 88,89 and 90 is that the effects of boron are consistently more severe in the presence of strontium than when either no modifier or sodium is employed. No explanation has been found regarding why this is so, however the similarity between the sodium and unmodified tensile strength results suggests that the variability in boron influence is not related to eutectic refinement as such, but rather to the effectiveness of strontium. This is supported by the modification MLR results which identify boron as highly detrimental in strontium modified samples, yet of no significance in samples containing sodium.

Variation in strength effects depending on the form in which boron additions took place was investigated. Figure 91 displays the tensile strength MLR residuals for strontium modified samples sorted according to the boron addition master alloy used. When it is considered that boron trends must be non-existent when no boron is present, it becomes obvious that no clear differences exist between the various boron additions. Initially it was expected that the supposedly inappropriate Al-3%B AlB_{12} master alloy would not produce results similar to those attributed to boron from the 5%Ti-1%B master alloy. This however does not appear to be the case, suggesting that the detrimental effects of boron exist irrespective of the boron addition method used.

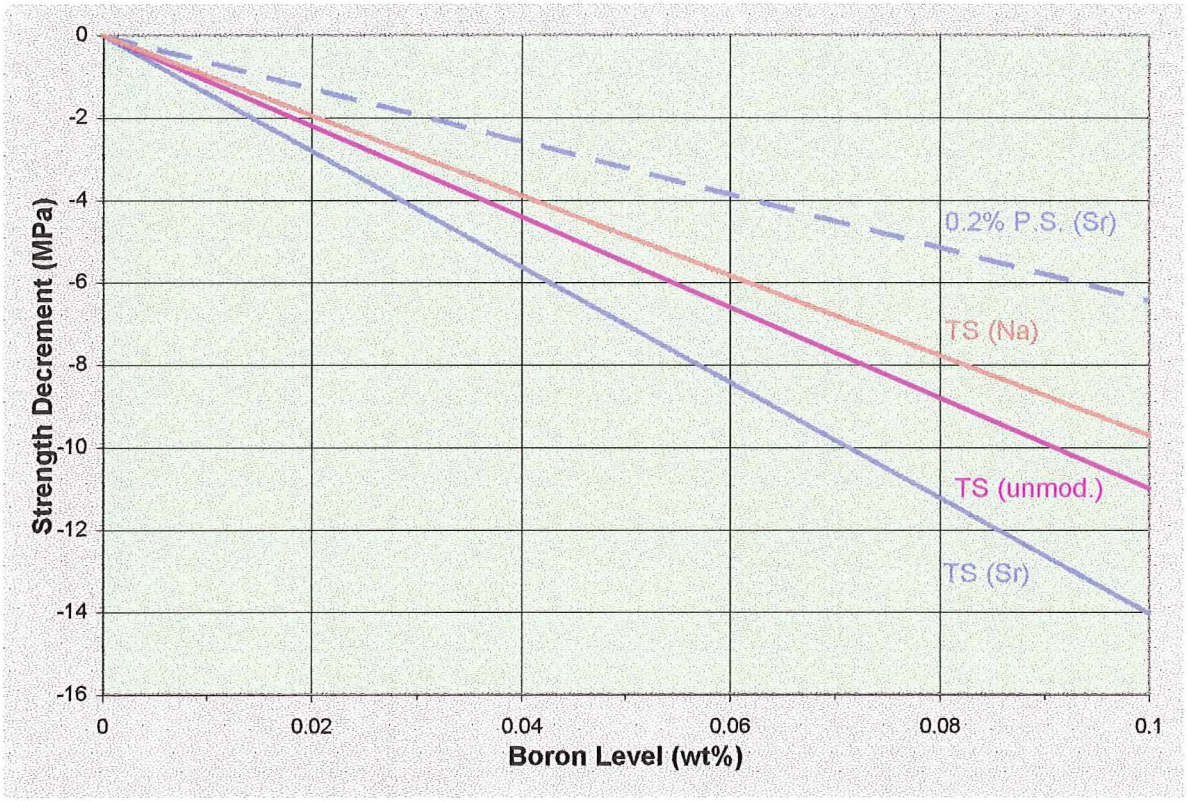


Figure 90: The effects of boron on tensile and 0.2% proof strength.

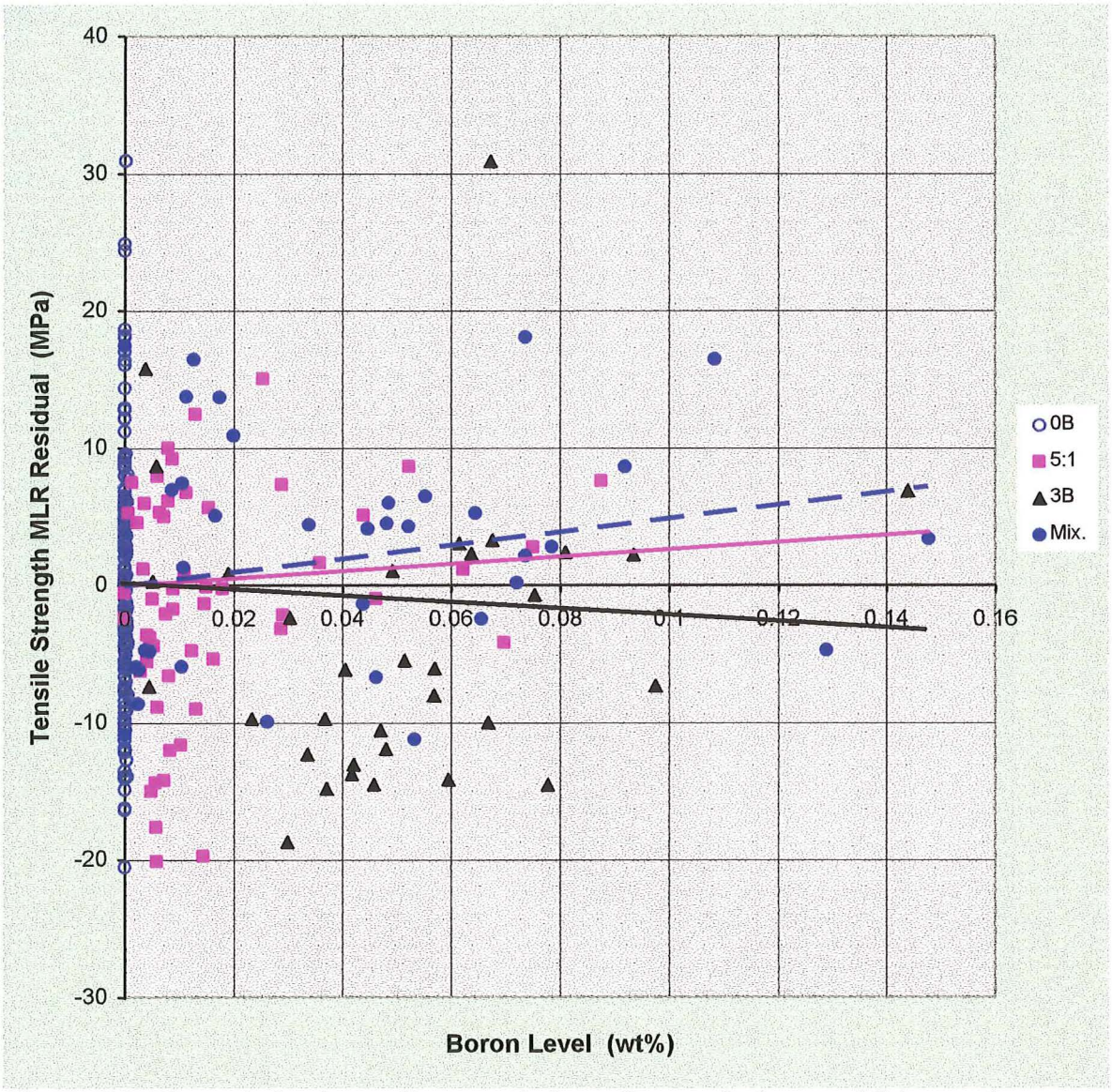


Figure 91: The variation in tensile strength depending on the boron additive used - strontium modified samples only.

8.3 ELEMENT INTERACTIONS

Without doubt all of the MLR analyses presented above could be improved if extensive effort was expended on identifying the complex element interactions which take place. As mentioned above, when interactions have been detected or suspected, efforts have been made to identify predictor variables capable of taking this into account. Accurately identifying suitable "link" functions is difficult since such functions often cannot be detected in simple two dimensional residual plots and, unless the interaction effect is substantial and the unexplained errors small, three dimensional residual plots also become virtually impossible to interpret. The following section outlines a process used to reveal a suspected but otherwise difficult to identify interaction between iron and manganese. The process by which the iron-manganese interaction was investigated proved extremely time consuming and serves to illustrate why limitations had to be placed on the effort expended on the individual analyses given in this report.

8.3.1 Establishing the Fe/Mn Hardness Interaction Characteristics

As mentioned in Section 2.6, iron and manganese are widely accepted as being strongly interactive. Manganese is credited with the ability to eliminate some of the detrimental effects experienced when high levels of iron alone are present. Since iron and manganese both had very significant effects on the hardness MLR results, attention was focused on accurately establishing the form of possible Fe/Mn interaction functions. Selecting the hardness data to confirm the interaction between iron and manganese proved fortuitous as this property correlated very well with the composition data which allowed reasonably sensitive determination of individual predictor values. A further point in favour of the hardness results is that they are largely independent of modification, so that all 495 observations could be combined into a single analysis set. The presence of an iron and manganese interaction was confirmed by separating the hardness MLR data depending on whether iron additions had been made and then comparing the influence of manganese via MLR analyses performed on the high and low iron observation sets. The manganese coefficients established by this work were statistically significant and totally incompatible

with each other, which proves that the degree of manganese-induced hardening is indeed influenced by the iron level. Following confirmation that a noteworthy and detectible interaction was occurring, the hardness data was subject to seven separate MLR analyses, each being based on samples containing varying ranges of iron and manganese. Three observation sets of varying iron level were used to establish the effect of manganese in each range. Similarly, four sets of data varying in manganese level established the average iron effect in each manganese range. The relevant results of this work are shown in Figures 92 and 93. The full MLR output data is contained in Appendix P.

Figure 94 schematically illustrates the effects of iron and manganese, individually, and in combination. The appropriateness of this figure relies on the major assumption that iron and manganese act in a consistent manner over each of the ranges in which their effects were established. For example, the average hardening due to manganese was established in three separate iron ranges yet the effects of manganese may not have been uniform over the 0-0.5% manganese range in each or any of the iron sets. It is the phase-forms* present and their amounts which determine the majority of cast specimen physical characteristics. Thus composition effects, and interaction functions, are largely a reflection of the differing phase-form constitutions which occur. The phase-forms in which both iron and manganese are present vary within each MLR composition range, therefore it is unlikely that the above assumption is complete.

Given the regression data available, the best way to accurately map the function depicted in Figure 94 would involve combining the calculated hardening effects of each iron and manganese phase-form with data from a suitable non-equilibrium phase diagram. The individual hardening effects of each phase-form could be found by firstly, calculating the average phase-form content of several of the MLR composition data set ranges, and then equating these amounts to the calculated average hardening increment. The composition ranges selected for generation of such expressions would have to be chosen with regard to the accuracy with which the average hardening could be assessed. Ignoring the effects of magnesium, five major iron and manganese phase-forms exist within the composition

* "Phase-form" relates to the various structures a phase may assume i.e. $FeSiAl_5$ may form as *eutectic* and/or *primary* needles.

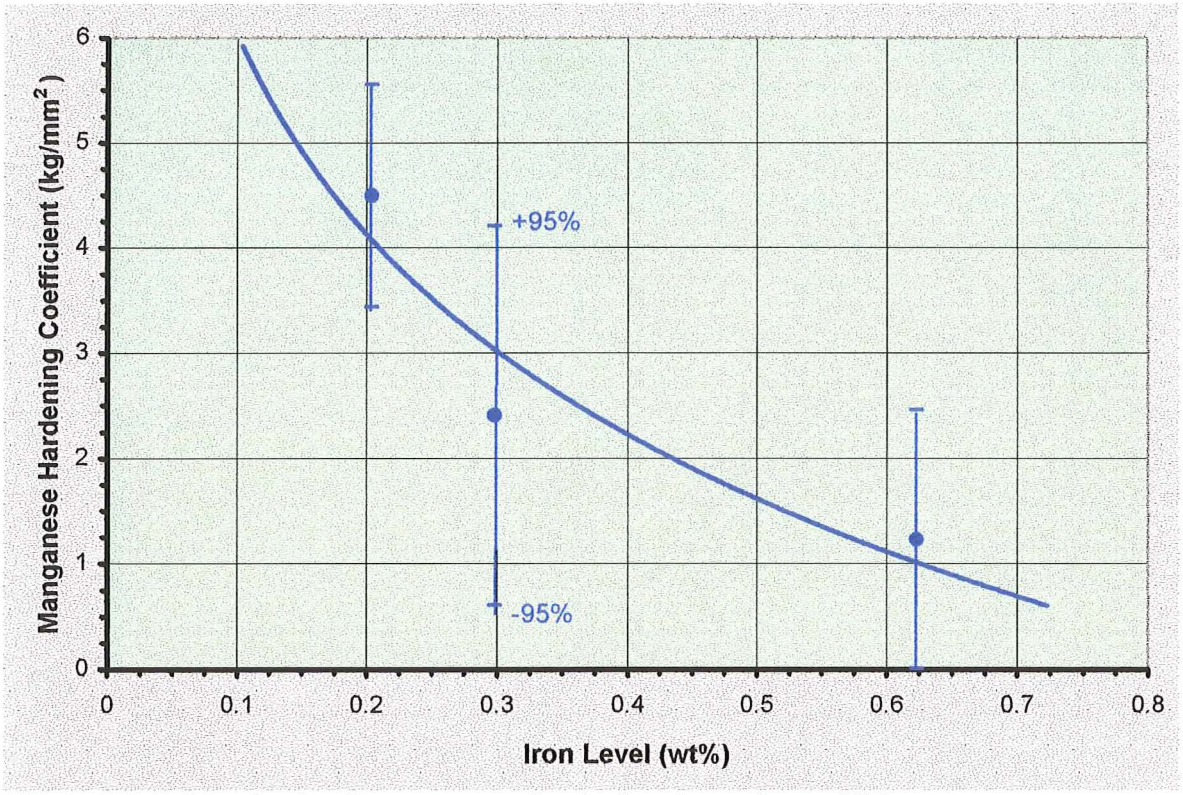
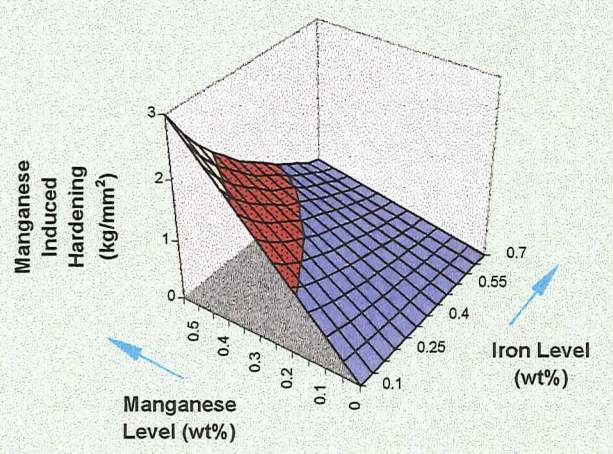
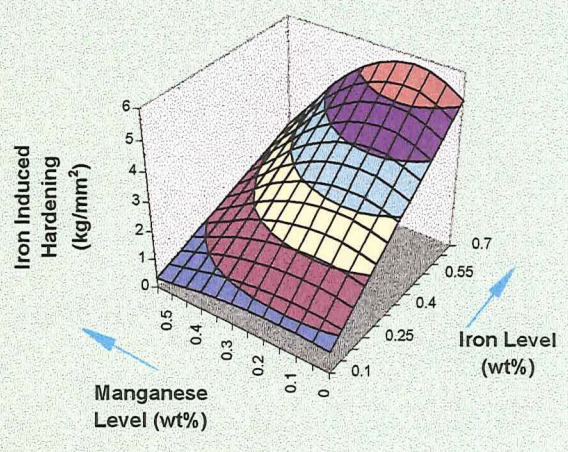


Figure 92: The reduction in manganese hardening due to iron addition.

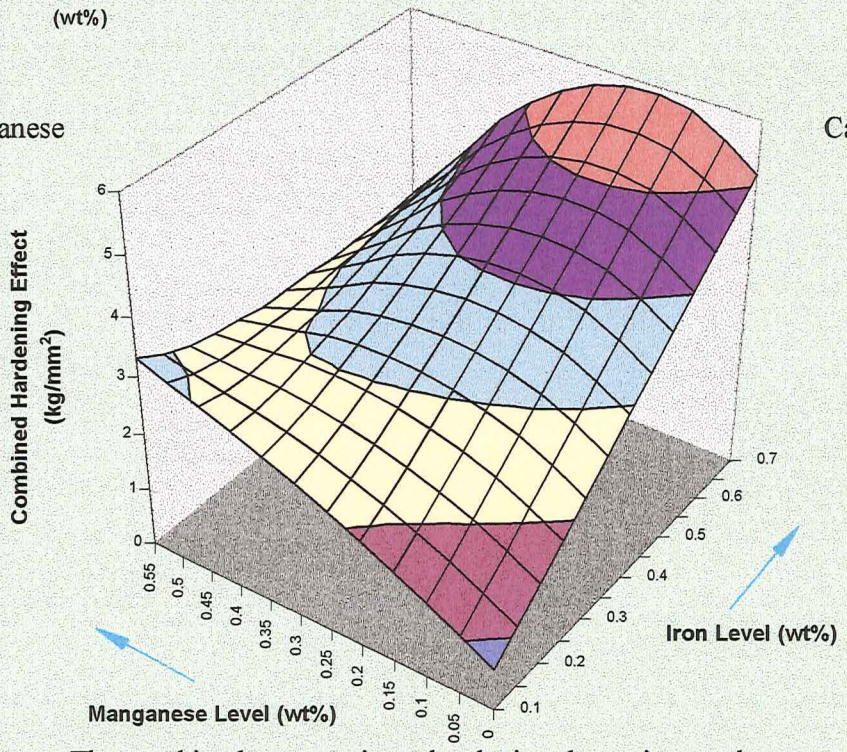
Figure 93: The reduction in iron hardening due to manganese addition.



Cast Specimen Hardening Due to Manganese



Cast Specimen Hardening Due to Iron



The combined cast specimen hardening due to iron and manganese

Figure 94: The hardening effects of iron and manganese as predicted by Figures 91 and 92 -c.f. Figure 61.

ranges investigated. Therefore five sets of phase-form versus hardening data would be required to generate a solvable set of simultaneous equations.

All of the above is only possible given the availability of a suitable non-equilibrium iron manganese phase diagram. Subsequent to the creation of a tentative phase diagram (see Section 8.3.2), an attempt was made to validate Figure 94 by the above process. The procedure described was found to be possible, however accumulated inaccuracies made the results of little or no practical significance.

Since Figure 94 was the best approximation of the iron-manganese interaction surface which could be found, mathematical functions capable of producing similar surface characteristics were tried in the full-data-set hardness MLR analysis. Each of these functions resulted in greatly improved statistical significance for the iron and manganese functions as well as the overall expression. The most significant interaction (or "link") term was of the $(Fe + x)Mn^2$ form and was significant to the 99.9999% level, hence the $(Fe - 0.05)Mn^2$ term used in the final hardness results given in Section 8.2.3.

An abbreviated but similar process was used to isolate the iron-manganese tensile strength interaction term.

8.3.2 The Need for Non-Equilibrium Phase Diagrams

As mentioned in Section 7.1, an MLR analysis can only establish direct relationships between the given predictor variables and the dependent variable of interest. Consequently, if interactions occur between the predictor variables which are not accounted for by the incorporation of accurate "link" terms, increased error reduces both the sensitivity with which influential factors may be detected and the significance of the results which are produced. Thus for optimum results, predictor variables must be selected which include all of the influential factors while being as independent as possible. For this reason, if the composition data used in this research could have been represented as the amount of each phase-form present, complex composition interactions would have been

virtually eliminated thus providing an excellent basis for accurate and intelligent MLR analysis. Removing predictor interactions via the use of phase-form contents would remove what is most likely the single largest compromise and source of error within the reported analysis processes. The results of a phase-form MLR would establish the effects of individual microstructural constituents and so have the potential to provide much more useful information than is currently possible, particularly in situations beyond the scope of the input data.

Implementing the process outlined above relies on an ability to readily convert conventional composition data into phase-form contents. The only way to establish phase contents would be through the use of relevant non-equilibrium phase diagrams which currently do not exist. Since the moulds (and hence cooling rates) used to produce Al-Si eutectic test bars are relatively uniform worldwide, suitable non-equilibrium phase diagrams would be widely applicable in industry as well as research. Obviously the generation of complete sets of phase diagrams could become exceedingly complex due to the number of known and potential interactions. If the major phase relationships of interest, i.e. Ti-B, Fe-Mn, Fe-Mg or Fe-Mn-Mg, etc could be established without excessively complex quaternary and higher-order interactions it is possible that such phase diagrams could be used to convert sample compositions directly into phase contents.

As mentioned in Section 8.3.1, during the generally unsuccessful attempt to validate the relationships in Figure 94, efforts were made to construct a tentative Fe-Mn phase diagram. The tentative diagram was initially generated using the approximate phase relationships listed in Table 3 and the comment by Mondolfo[78C] that, when the combined iron and manganese levels exceed 0.8%, further $(FeMn)_3Si_2Al_{15}$ crystals are primary. Since this diagram was approximate at best and made no concession for variation in cooling rate it was adjusted so that it would be representative of the microstructures displayed by several (17) select cast specimens. It should be noted that none of the samples selected for this microstructural analysis contained magnesium hence the approximate diagram shown in Figure 95 is devoid of magnesium-induced complications. The adjustments which were made imply that:

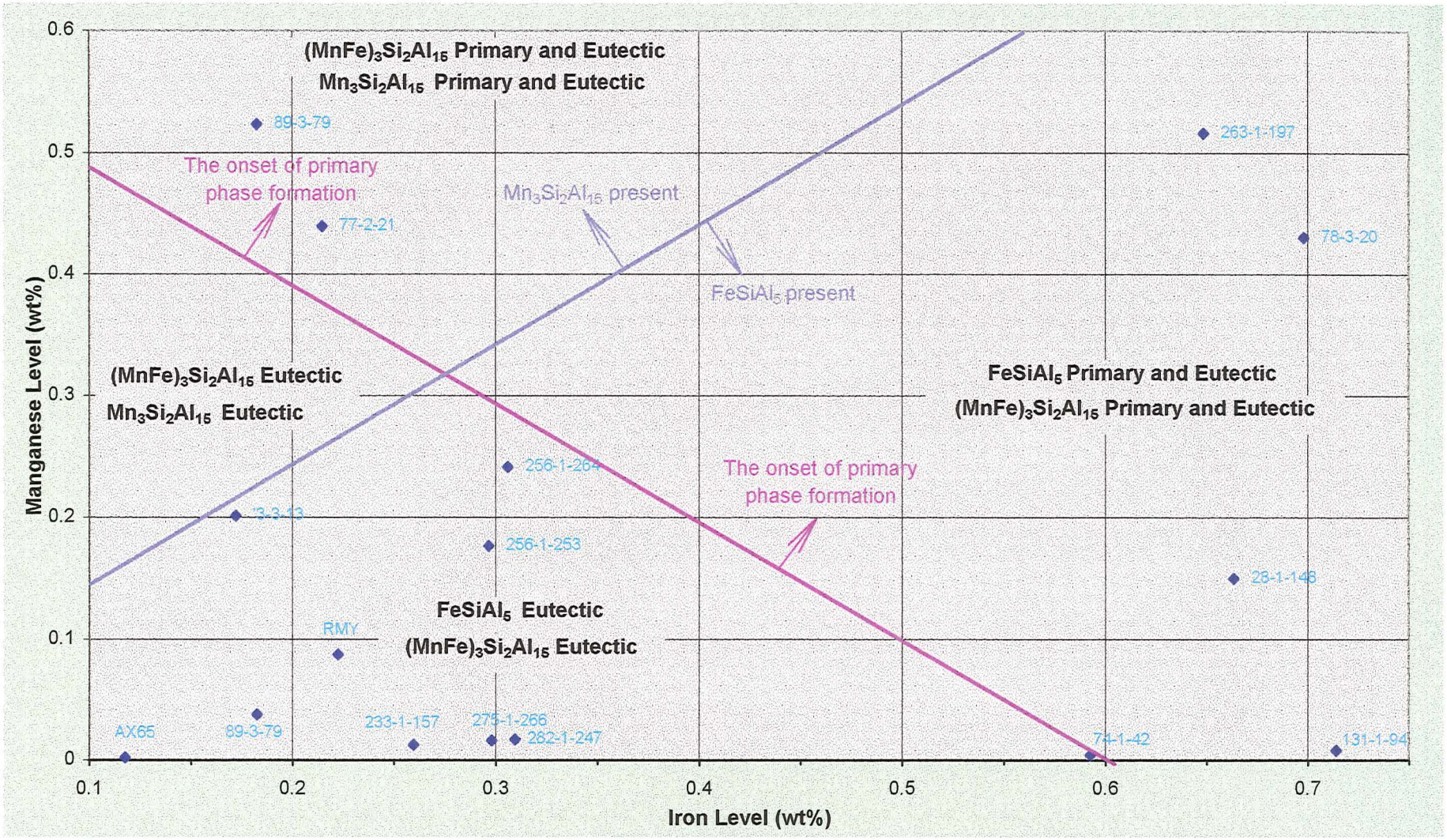


Figure 95: Tentatve iron-manganese non-equilibrium phase diagram - constructed using the data given in Table 2 and the phase characteristics observed in the microstructures of the indicated samples.

- ≈ 0.05% manganese is required before manganese containing precipitates are observed.
- All iron is present as $FeSiAl_5$, none being held in solution.
- Primary iron precipitates form as soon as iron levels exceed 0.6%.
- Primary manganese phases form when manganese levels exceed 0.48%.
- If the Fe/Mn primary phase relationship is linear, iron, manganese and the combined phases become primary according to the following relationship:

$$1.25Mn\% + Fe\% > 0.6$$

Apart from the obviously large margins for error associated with the tentative diagram, one major assumption was made when the average phase-form contents were calculated during the work described in Section 8.3.1. This assumption was that over the composition range of interest, the effects and interactions of iron and manganese are not influenced appreciably by variation in other elements. The elements most likely to invalidate this assumption are the modifiers and magnesium. As shown in Figures 76,77,78 and 79, evidence exists that the modifiers do influence the iron-manganese interaction effects. This influence does not seem to have stemmed from modification per se or an obvious change in the appearance of Fe/Mn phases (the latter point does, however, deserve more rigorous investigation). It is also known that magnesium present in foundry alloys commonly forms $FeMg_3Si_6Al_8$, suggesting that Fe/Mg interactions may exist to complicate the Fe/Mn interactions. Mondolfo[78C,G and H] suggests that whenever iron levels exceed those of magnesium - as is always the case in this research - $FeMg_3Si_6Al_8$ forms. If this reaction goes to completion with less than 25% excess iron then even at the minimum iron and maximum magnesium levels investigated, the magnesium will be entirely in the form of iron-magnesium silicide. It then becomes a question of whether manganese displaces the magnesium and, if so, to what extent. No data would appear to be available on this subject. These factors all indicate that a ternary phase diagram may be necessary to accurately assess the phases present in alloys containing iron, manganese and magnesium in combination.

Although attempts to validate Figure 94 using an approximate phase diagram devoid of the complications discussed above was largely unsuccessful, this does not confirm that Figure 95 is in fact inaccurate or was inappropriate, although this possibility is highly likely.

8.4 PHYSICAL PROPERTY INTER-RELATIONSHIPS

The significance of inter-relationships between the various monitored mechanical and structural properties was also investigated using MLR analysis. Most of the findings resulting from this work are of little practical significance, hence they are not provided in full numerical detail.

(A) Tensile Strength

As could be predicted by the close relationship displayed between the modifying elements and tensile strength, modification ratings show strong correlation with strength. The modification rating alone is insufficient to allow accurate prediction of attained strength; it does however, allow average predictive errors to be reduced by nearly 50% compared to the use of a simple mean strength value. Hardness and porosity levels are also influential in strength determination with the relationship shown below having a correlation factor of 73% and a minimum predictor significance of 99.4%.

$$TS\ (MPa) = -0{\cdot}715.(\text{AFS mod rating} - 9)^2 + 0{\cdot}786.\text{Hardness}\ (kg/mm^2) - 4{\cdot}96.\text{Porosity Area}\ (\%) + 126{\cdot}806$$

This relationship serves little practical purpose; it does, however, illustrate that functions relating strength directly to hardness, as are often quoted for the fine structures encountered in most wrought products, are inappropriate for this material. Grain refinement has a poor correlation with tensile strength which is in agreement with the findings reported by Mondolfo[78E] and others as mentioned in Section 2.3. The TS results presented in Section 8.2.5 indicate that boron and titanium have differing effects on strength and thus the overall finding that grain refinement is ineffectual in influencing strength may be a compound effect rather than being

strictly correct in each case. Separate MLR analyses were performed on the strength data from samples with and without boron. Unfortunately, the results from these analyses were inconclusive as once again the grain refinement terms displayed no statistical significance.

(B) 0.2% Proof Strength

None of the measured structural and mechanical properties were found to be closely related to proof strength. Hardness readings were statistically very significant predictors in the estimation of proof strength yet the actual predictive improvement was no more than 10%. None of the remaining properties, including tensile strength, were significant predictors even at the 85% level.

(C) Elongation at Fracture

Elongation values were found to be closely related to tensile strength, hardness and grain size with the following expression able to reduce predictive ductility error by 71%, i.e. $R^2 = 0.713$.

$$\delta L(\%) = 0{\cdot}1244.TS\ (MPa) - 0{\cdot}4543.Hardness\ (kg/mm^2) - 0{\cdot}101.Grainsize\ (ASTM\ G(M)) + 12{\cdot}45$$

Ductility is a controlling factor in the failure of several compositions within the BS1490-LM6 composition range, and modification effects both tensile strength and ductility in a similar way, thus it is not surprising that ductility and tensile strength are closely associated. Clearly high ductility, which is only available in well modified structures, is a prerequisite for high strength. Hardness was found to be inter-related to ductility in two ways; ductility and ductility variation decreased markedly as hardness increased (i.e. this predictor is heteroscedastic). The influential effects that grain size has on ductility indicate that reduced grain size causes noticeably reduced ductility.

As with tensile strength, the idea that grain size per se influences ductility is difficult to substantiate as it is impossible to separate the influence of the grain-refining additives from the actual grain refinement. It is highly likely that grain size refinement has beneficial ductility effects which are outweighed by detrimental side

effects from the boron and titanium additives themselves. The results presented in Sections 8.2.4 and 8.2.5 show that for a given degree of refinement, influences of titanium and boron on mechanical properties are quite different, supporting the theory that it is not grain refinement as such which dominates the observed property variations.

(D) Modification

The modification results presented in Section 8.2.1 prove that titanium promotes modification while boron has the opposite effect. These findings were further confirmed by the results of linear regression analysis relating modification and grain size. Samples subject to titanium-induced grain refinement displayed a minor but significant positive correlation between modification and grain size. Boron-refined samples displayed a similar but negative correlation. The methods by which titanium may influence modification are briefly mentioned in Section 9.4

9.0 DISCUSSION OF THE MLR-DERIVED RESULTS

9.1 SILICON

It could be expected that the 30% increase in eutectic silicon phase level which occurs between 10 and 13% silicon would also necessitate that modifier levels rise by a similar proportion to maintain optimal modification. This assumption is supported by comments by Schulz[179] and Closset and Gruzleski[18X]. Schulz reports that the optimum sodium content rises from ~0.006% at 6% silicon to 0.009% at 13% silicon. Closset and Gruzleski suggest modifier contents should be increased by 80-100% when silicon levels are increased from 7 to 12.5%. Surprisingly, the results of the present research do not support these findings as the only silicon/modification interaction detected occurs at high boron levels when the detrimental influence of boron increases as silicon levels rise (see Figure 48).

If, for a given modification level, the alloys monitored in this investigation had required modifier content variations of similar magnitude to the displayed silicon variation, i.e. ±>20%, the expected modification range would be similar to that displayed in Figure 96. As Figure 96 shows, the expected modification rating would vary by as much as 1-1.5 modification units between high and low silicon levels. The modification-MLR iron terms were statistically significant with maximum induced variabilities of only 0.2 and 0.5 modification units (*p*-values 4% and 0.001% respectively). Thus had a silicon/modifier interaction of the above magnitude occurred a silicon/modifier MLR predictor term of exceptionally high statistical significance should have been evident.

The conclusion which can be drawn from this is that to maintain a given modification state for a given increase in silicon level, modifier levels do not need to be increased by more than ≈33% of a proportionally similar amount.

It is interesting to speculate as to why there is a need for no or very little additional modifier when silicon levels rise. One possibility which has been considered is that the primary aluminium dendrites solidify with appreciable sodium in solid solution. Sodium

contained within primary dendrites will effectively be trapped and unable to take part in later eutectic refinement. If modifier contents within the aluminium dendrites had reached at least two thirds the amount required for optimum modification, it is possible that the resulting silicon/modification interaction would be smaller than could be reliably detected by the MLR analysis performed. Reducing the amount of primary aluminium by adding silicon increases the amount of eutectic to be modified but may also increases the amount of modifier which is no longer "trapped" within the aluminium dendrites. The amount of additional modifier required to offset increased silicon levels therefore depends entirely on the solid solubility of the modifier in the solidifying silicon-saturated aluminium dendrites. If the solid solubility limit is close to the threshold required for eutectic modification, minimal additional modifier will be needed. As mentioned above, the results of this study suggest that when silicon levels rise, the levels of modifier required increase by, at most, one-third of that which would be expected. This indicates that the modifier solid solubilities are more than two-thirds the optimum modification threshold levels. The implied sodium and strontium solid solubilities are thus at least 0.008% and 0.016% respectively.

Summaries of existing Al-Na and Al-Na-Si equilibrium phase data have been provided by Mondolfo[78J&78K] and Bochvar et al[180]. The comments by Mondolfo regarding sodium solid solubility stem mainly from two works, one by Schulz[179] and the other by Ransley and Neufeld[181]. Each of these studies are somewhat dated, having been published in 1948 and 1950 respectively. Ransley established the solid solubility of sodium in aluminium-silicon alloys over the temperature range 500 to 600°C. This was achieved by conducting tests in which dissolved sodium was always in equilibrium with the ternary AlNaSi phase termed τ. Since τ-phase does not occur during non-equilibrium solidification of primary aluminium in eutectic type alloys, the 0.0016-0.0005% solubility factors established by Ransley and quoted by Mondolfo must be regarded as conservative and most likely inappropriate for most practical situations. In the same sentence that Mondolfo reports Ransley's findings, he reports the differing findings of Shulz, namely that sodium solid solubility at the eutectic temperature is 0.002-0.003%. The exact method by which Schulz obtained her 0.002/0.003 range is unclear, hence these results must also be treated with caution. A phase formation table given by Mondolfo[78H], which is largely reproduced in

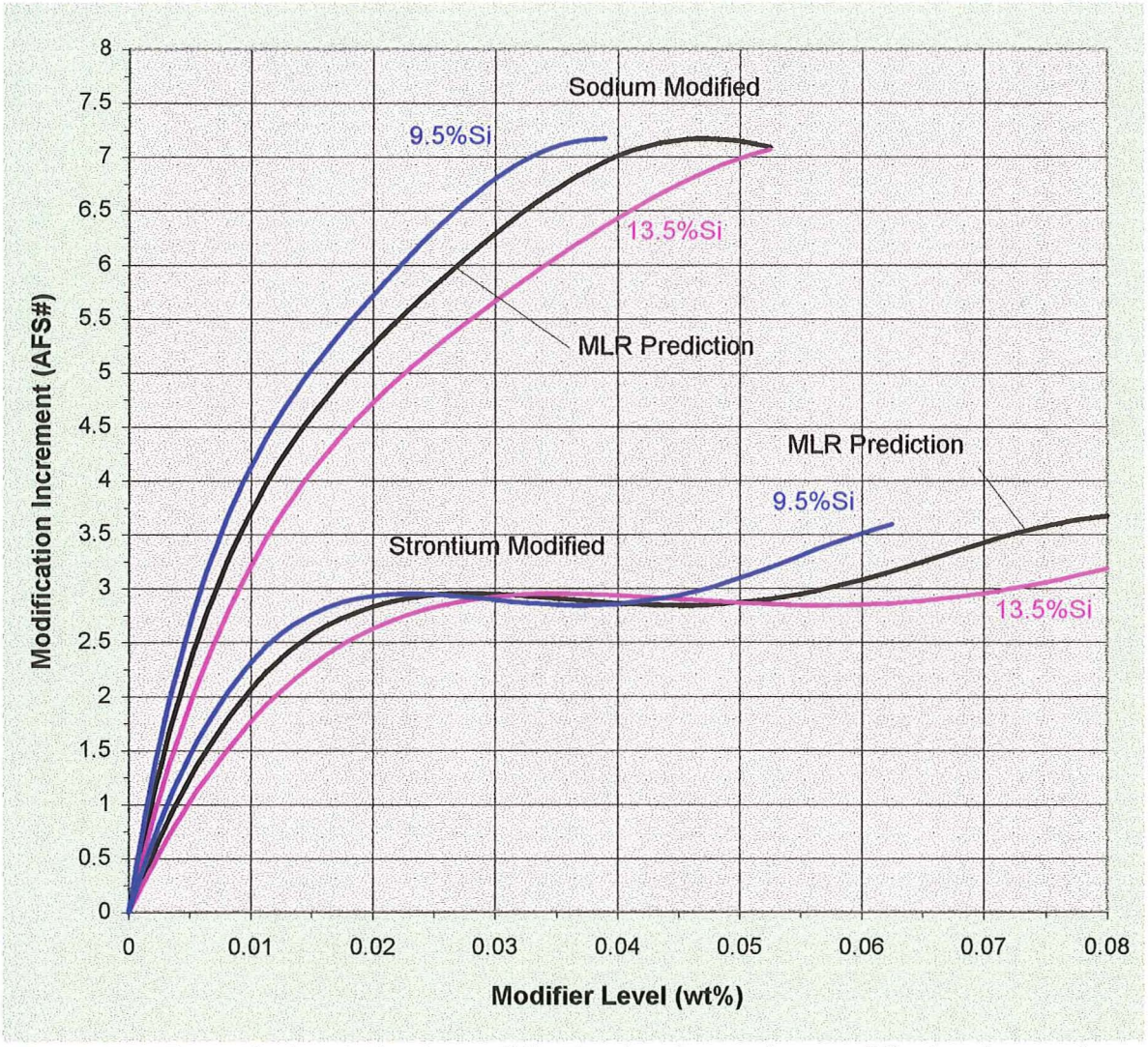


Figure 96: Theoretical variation in modification level assuming modifier levels must be proportionally similar to silicon level.

Section 2.6 (Table 3), implies that sodium solid solubility is approximately ≈0.01%. Unfortunately, the source of this figure is not provided, hence it may only be regarded as an estimate.

The more recent review by Bochvar et al[180] draws on several works, including those of Schulz, Ransley and Mondolfo. Bochvar makes only one comment on the solid solubility of sodium in systems which are not at equilibrium with τ, that being that 0.023 at% (0.02 wt%) Na may be held in solution within pure aluminium below the 660.45°C solidification temperature. Bochvar et al's comments come from a 1990 work by Massalski[182] which Bochvar et al have misquoted via a transcription error. Massalski actually quotes that the solid solubility of sodium is 0.0023 at%, this figure originating from the work by Ransley quoted above! It is obvious that very little original work has been conducted on the Al-Na and Al-Si-Na systems with one or two reports by authors such as Ransley in the late 1940's providing the only substance to most subsequent reports.

As made clear by the above statements, ternary phase information regarding the Al-Na-Si system is far from comprehensive and much of what has been reported is either open to question or has been misrepresented in subsequent publications.

No information would seem to exist on the solid solubility of sodium in silicon-saturated aluminium (Al-1.5%Si) which is somewhat surprising as this is the approximate composition of the aluminium which solidifies within the eutectic and primary dendrites of virtually all commercial alloys subject to sodium modification. The absence of this information coupled with the indistinct nature of the sodium solid solubility data which does exist, prevents conclusive confirmation of the sodium solubility limits implied by the modification MLR results.

Specific information regarding the solid solubility of strontium in silicon-saturated aluminium is also difficult to obtain. Al-Sr binary phase information provided by Hansen[183] suggests that "negligible" strontium may enter solid solution with aluminium. This agrees with comments by Closset et al[28] that strontium solid solubility is "not appreciable", however solubility of only 0.005 at%Sr is needed to agree with the MLR

implications - a figure which may well appear "negligible" or "not appreciable". A review of ternary Al-Si-Sr phase information by Ferro et al[184] includes a ternary isothermal section at 500°C originally proposed by Ganiev et al[185] in 1977. This diagram suggests that strontium may be soluble to levels as high as 1.0% within pure aluminium and that strontium solid solubility varies little in the presence of silicon. It is clear that no conclusive information exists regarding the true bounds of the single phase aluminium/strontium phase region, hence once again, no confirmation or dismissal of the MLR implied solubility limits can be made.

The effect of silicon variation on porosity was found to be minimal. The sodium modified samples displayed a very slight decrease in porosity as the silicon level increased, this effect was however not conclusive. As silicon variation between 9.5 and 13.6% is unlikely to have any significant influence on gas adsorption or absorption, the major factor relevant to porosity is shrinkage variation. The internal shrinkage data provided by Burt[6], which was discussed in Section 2.4.1, suggests that over the silicon range of interest, internal shrinkage varies only very slightly, which supports the MLR findings.

As would be expected, increasing the already substantial silicon levels by up to 42% has a major hardening influence on cast aluminium-silicon eutectic alloy. The approximate hardening index for silicon was found to be 1.2 kg/mm^2 per wt% silicon added, which is considerably less than the indices established for iron and magnesium (≈7.5 and >40 respectively). As Figures 58 through 64 show, the large silicon range permitted by BS1490-LM6 allows silicon to be just as significant in hardness variation as any of the other composition variables. Surprisingly, the form the silicon adopts, which is a dominant factor in strength and ductility levels, has little or no influence on hardness.

Initially, it was thought that the very small volumes of primary aluminium which occur when silicon levels exceed ≈12.5% would make grain size measurement difficult. However, the modification-induced eutectic shift effectively eliminated this problem in all but a few samples. Prior to analysing the grain size data it was expected that problems would be encountered in the silicon region corresponding to the results from eutectic and hypereutectic samples as the grain size definition effectively changes in this region depending on the modification state. This problem did not produce the inconsistencies

anticipated, hence it can be concluded that the differing grain size definitions are reasonably compatible in the critical eutectic transition region. Clearly, the eutectic colonies in marginally hypereutectic samples are similar in magnitude to the primary dendrites found in slightly hypoeutectic samples.

As Figure 68 (given in Section 8.2.4) shows, increased silicon content reduces the grain size until fully eutectic structures are encountered. This effect is no doubt due to the lower temperatures and shorter periods over which primary solidification occurs when the silicon levels rise. In the actual eutectic region, silicon variation is shown to have virtually no effect on grain size. This may be correct, but it is more probable that primary dendrites continue to become smaller and more numerous in fully modified structures while eutectic colonies grow larger in hypereutectic (hence unmodified) equivalents. Had samples been analysed at higher silicon levels, it is expected that the onset of colony growth would become obvious due to the higher temperatures at which nucleating silicon crystals would begin to form.

The effects of silicon on the measured tensile test parameters were illustrated in Figures 72 and 73. These results clearly show that the effects of silicon on tensile strength depend on the presence of modifier and which modifier was used. The fact that silicon has a varying effect depending on the presence of a modifier, indicates that the silicon and modifier effects are linked in some way, yet as mentioned in Section 8.2.5, no significant "link" functions could be found. The lack of a significant "link" function indicates that minimal modifier is required to change the silicon effects and that when modifier levels exceed this amount no further notable interaction occurs. The lack of a silicon/modifier term also supports the theory proposed above, that over the silicon range of interest modification effects are independent of silicon level.

All of the effects of silicon displayed in Figure 73, and the lack of a significant "link" term, may be explained if very minor levels of modifier are sufficient to increase ductility such that the embrittling effects of silicon are no longer dominant in influencing the tensile strength. When modification is not carried out, initial ductility is extremely low, hence when this factor is compounded by the addition of more silicon, strength is adversely effected. If the dominant ductility constraints can be alleviated, the substantial

strengthening effects that silicon has on proof strength may be carried through to higher tensile strengths. Minor additions of sodium are sufficient to completely prevent silicon-induced embrittlement from controlling the tensile strength results of samples containing less than 11.5%Si. Ductility gains due to strontium addition are not as pronounced, thus in this case, the embrittling effects of silicon are initially counteracted but never entirely overcome. When either modifier is present, the effect of silicon additions on tensile strength is greatly improved compared to their absence. As Figure 72 shows, gains in proof strength are small beyond 11.2-11.5%Si, hence tensile strength gains due to the increased proof strength are rapidly outweighed by ductility losses which are substantial at these high silicon levels. If these assumptions are correct, the tensile effects of silicon additions are largely dependent on the ductility of the structure to which the additions are made.

The tensile property results displayed in Figure 73 are in excellent agreement with the tensile strength, yield strength and ductility charts provided by Harris et al[139] and Charbonnier et al[140], mentioned in Section 2.6. This finding highlights the injustice Kashyap et al[138] have done to Harris et al[139] by stating that the earlier authors' results show "negligible" variation in tensile properties between 4 and 13%Si! Harris et al investigated modified and unmodified sand cast alloys varying in both magnesium and silicon over the 0.1-0.3% and 4-13% ranges respectively. When the unmodified silicon variation results are projected so as to represent 0%Mg content, the resulting trends and their magnitudes are virtually identical to those shown in Figure 73. The modified sample results provided by Harris et al are of little practical worth as the sodium *addition* amounts were recorded but the actual *retained* sodium levels were not, due to the unavailability of suitable analysis methods. Mondolfo[78B] quotes nine references which report that silicon increases strength at the expense of ductility, which is in agreement with the findings of this research, *provided* the composition range in question is not subject to severe ductility limitations.

9.2 THE MODIFIERS (Sodium and Strontium)

The effects of the conventional modifier elements have been discussed in detail throughout this report. While controversy still surrounds virtually every issue related to modification, when the influence of variables such as local cooling rate, phosphorus level, modifier addition type and magnesium content etc are taken into account, it is not surprising that no two sets of experimental results seem entirely compatible. When consideration is given to these different casting variables, the quantified results given in Chapter 8 (Figs. 46, 47, 53, 67, 74, and 75) seem to be mostly in accordance with what could be expected.

As far as modification is concerned, the greatest degree of eutectic refinement correlated well with optimised mechanical properties. The only notable point on this issue is that, as already mentioned, determining the optimum strontium modified structure is not easy by metallography alone. As Figures 46 and 47 show, strontium is not able to produce the same degree of eutectic refinement as sodium. This is in agreement with comments in the ASM Aluminium Handbook[133D], and those by Anon[144] and Gruzleski and Closset[18B]. The variation in the effects of sodium and strontium are considerably more pronounced in the results of this research than is usually indicated. This is thought to be due to a combination of two factors. Firstly, most modifier comparisons have centred around alloys containing less silicon (eg LM25), thus the observed effects and variations in modification are not as pronounced or as critical. Secondly, as noted in the above mentioned texts[133D & 18B], eutectic refinement by strontium substantially improves with longer melt exposure times than those used in the present work. The second point is particularly relevant as, even though the strontium master alloy used is claimed to be effective within 1-2 minutes (see Section 5.2), the melt exposure time of approximately 5-6 minutes is much less than would normally be encountered.

No information could be found relating mechanical property gains to strontium level for eutectic alloys. However, the shape of the tensile strength variation plot is very similar to that provided by Das Gupta et al[43], who studied cast Al-6%Si-Cu. Optimum properties are obtained with 0.025-0.04% strontium, which is in general agreement with comments by numerous authors including the strontium master alloy producers[29], who indicate that up to

0.05% may be required. What Figure 75 does highlight is that the commonly reported opinion that strontium does not cause overmodification problems is quite untrue at eutectic silicon levels.

The data found in the literature relating tensile properties to sodium level reproduced in Section 2.6 (Figure 22) is thought to be schematic, yet the only significant difference between this plot and the actual results in Figure 74 is the magnitude of the tensile strength gains. Strength gains of 65% ($\approx$ 65 MPa) have been quoted by Pillai et al[186], however these same authors quote modification-induced hardness increases of over 6 $kgmm^{-2}$, which is clearly not the case in the present work. One finding which was unexpected and previously unreported is that ductility increases noticeably when severe sodium over-modification occurs. This ductility increase is not accompanied by increased strength, indicating that both the strengthening and embrittling effects are greatly reduced by the formation of non-faceted primary silicon crystals. A similar effect is not observed with strontium overmodification as the Al_2Si_2Sr which forms appears to draw strontium from surrounding areas causing a reversion of the eutectic to a coarse form

The porosity MLR results were not entirely as anticipated or as could be expected commercially. The fact that sodium is detrimental, particularly when added at levels beyond 0.01-0.015%, was expected as the form of the sodium addition was far from ideal. In situations where metallic sodium is added in vacuum sealed canisters contamination by hygroscopic reaction products and storage oils would be practically non-existent and hence, the degree of sodium-induced porosity would be somewhat lower than was found in the present research. Initially, it was expected that strontium additions would contribute to the production of less sound castings yet, as the results in Section 8.2.2 show, this was not the case. Strontium had minimal influence on the measured porosity levels. Several authors have linked strontium modification with increased porosity; consequently, this has been the subject of detailed research reported as recently as March 1995[178]. Strontium definitely increases porosity in Al-7%Si-Mg alloys, however this is not due to increased gas content but rather modified solidification characteristics and possibly increased inclusion levels. Most porosity associated with strontium addition is micro-porosity thus alloys prone to micro-shrinkage exacerbate the problem. Of the 8.6% volumetric contraction which occurs on solidification of Al-7%Si-Mg alloys, 0.4% occurs as micro-

shrinkage. Al-11%Si alloys contract only 7%, none of which is microshrinkage[76]. When these factors are combined with the results of this study it seems unlikely that the Al-10%Sr master alloy introduces inclusions. It is however, possible that strontium and magnesium interact to provide pore nucleation sites. This latter point is supported by the finding that magnesium-induced porosity is somewhat worse in the presence of strontium than sodium (see Figure 54).

As is immediately obvious in Figure 67, the modifying elements have somewhat different effects on cast grain sizes. Strontium has a slight coarsening effect which can virtually be ignored at conventional modifier levels. This is in agreement with a statement by Appelian[187] that *"strontium has no grain refining capabilities"*. Sodium has a far more pronounced effect, although again at conventional addition levels it assumes little importance. No reference has been found regarding the effects of sodium on grain refinement, however this research has proven sodium to act as a mild refiner. This may be due to improved aluminium nucleation which should be obvious in thermal cooling data. Of the numerous investigations performed into the effects of modification on thermal cooling characteristics, only one was found which noted primary aluminium nucleation at higher temperatures. The authors in question[24] concentrated specifically on sodium modification and were certain that modification resulted in early nucleation of aluminium but had no effect on the eutectic arrest temperature. The latter point runs contrary to the findings of almost every other pertinent report, hence the former is also open to question. If sodium does not aid primary dendrite nucleation then it may retard dendrite growth thus enabling more nuclei than normal to become active. This theory is supported by the reported observation that aluminium solidification becomes more faceted in nature in the presence of a modifier (see Section 2.2) but does not explain why strontium does not act in a similar manner.

The interactions between the modifiers and magnesium, iron and silicon are dealt with in the following sections.

9.3 COMMON IMPURITIES (Iron, Manganese and Magnesium)

Magnesium

As was discussed in Sections 8.2.1 and 8.2.5, magnesium is detrimental to modification and consequently, is also detrimental to strength and ductility. Magnesium acts to counter modification by causing detrimental effects which are proportional to both the modification effects and the magnesium level - see Figures 46, 47, 83, 84 and 85. Should the detrimental effects of magnesium continue in a similar manner from 0.1 to 0.3% Mg as they do from 0-0.1%, modification should cause little or no improvement in the strength of 0.3% Mg alloys. This is in agreement with results presented by Harris et al[139] and numerous other authors who have investigated the Al-7%Si-Mg alloys.

Magnesium has been shown to form $FeMg_3Si_6Al_8$, which is associated with undermodified bands of coarse silicon, see Plate 24. The undermodified bands persist even when overmodification is evident in surrounding regions, hence the inherent embrittling and weakening effects cannot be avoided by increased modifier additions. As the undermodified bands occur generally irrespective of excess modifier levels, all modification ratings are reduced including those associated with optimum properties. Interestingly, optimum modifier levels are unaltered by the presence of magnesium. Since sodium causes more pronounced silicon refinement and property variations than strontium, the detrimental effects of magnesium are similarly more pronounced in sodium containing alloys. As no comments regarding reduced microstructural homogeneity have been found it may be that magnesium-related effects vary depending on modifier exposure periods. If modifier exposure times are significant in determining magnesium effects, magnesium levels and modifier incubation periods may be closely interrelated - this issue deserves future investigation. Bercovici et al[34] have investigated the microstructural effects of magnesium on foundry alloys and in agreement with the results given by the present study, concluded that magnesium acts in a very similar manner to phosphorus by reducing the effectiveness of conventional modifying elements. Bercovici et al suggest that the detrimental effects of phosphorus may be enhanced by the presence of magnesium, which seems feasible if magnesium can 'tie-up' modifier which would otherwise neutralise silicon-nucleating AlP. In the absence of conventional modifiers magnesium, unlike

phosphorus, has little or no effect on eutectic coarsening. This finding is in agreement with comments by Rooy[188] and supports Bercovici's proposed phosphorus/magnesium/modifier interaction.

Charbonnier et al[140] have produced results which show that magnesium additions to modified Al-11%Si alloy decrease ductility which is in agreement with the results produced here. Charbonnier et al also show that marginal strength increases occur in alloys particularly low in phosphorus, something which has not been reiterated in the results produced here. As was shown in Figure 86, in the absence of modification, magnesium is beneficial to strength. This suggests that the magnesium phase itself increases strength but that the modifier interaction rapidly eclipses this effect.

The hardness and porosity results also show that a very significant magnesium/modifier interaction occurs. In this case the average increase in hardness due to magnesium was approximately 67% higher in the presence of strontium than in the presence of sodium. Porosity due to magnesium was substantially worse in strontium modified alloys than those containing sodium. No published information has been found to corroborate these results, however, given the statistical significance associated with them, no room for doubt exists.

Iron

No significant porosity or grain size effects were attributed to iron. No publications could be found to dispute these findings. The only references relating iron to either of these properties were by Mondolfo[78F] and Apelian and Cheng[187]. Mondolfo states that iron reduces the solubility of titanium and boron and so improves grain refinement due to the addition of either of these elements. No statistically significant iron/titanium or iron/boron terms could be found to substantiate these findings. Apelian and Cheng found that additions of 1.5% iron to Al-7%Si alloy caused very minor reductions in grain size. Following rather limited experimentation these same authors found that iron has no effect on eutectic refinement, as did Bercovici[34]. These findings do not agree with later results published by Jaquet[42], who found that iron coarsens the eutectic in strontium modified Al-7%Si alloy which is in agreement with the MLR derived results given in Section 8.2.1. Unfortunately, no information has been found relating sodium modification to iron level thus the beneficial effects alluded to in Section 8.2.1 cannot be substantiated by

independent results. Statistically, the possibility of iron being beneficial to sodium modification is very high. Since iron has opposing modification effects depending on the modifier used, the implication exists that a significant iron/modifier interaction takes place.

KBM[29], the strontium additive manufacturers, state (without elaborating) that evidence exists supporting a significant iron-strontium interaction. KBM suggest that the strontium-iron interaction may reduce the embrittling effects of iron, something which is supported but not substantiated by the results given in Section 8.2.5. No quantified results relating iron level to Al-Si eutectic alloys have been found, however characteristic tensile curves for iron in an Al-7%Si-Mg alloy have been provided by Kashyap et al[138]. These results show that as iron levels rise so do the proof strength and tensile strength. The TS gains are only compromised by ever decreasing ductility. These same characteristics are shown by the results due to iron and silicon produced in the present research. The major difference between the characteristics due to iron and those due to silicon is that, below the 0.6% iron limit imposed by BS1490-LM6, iron induced embrittlement is far less pronounced, hence strength gains are not compromised in the same way. Since iron-related proof strength gains are independent of the modifier used (as is hardness), it would be expected that maximum iron-related TS gains would be associated with the modifier linked to the lowest iron-induced embrittlement. This has proven not to be the case as strength gains and ductility losses are greatest in the presence of sodium. This may well be due to strontium possessing an ability to reduce iron embrittlement as suggested by KBM, or more likely it is simply a reflection of sodium-containing alloys having substantially higher inherent ductility.

The reported findings of Kashyap et al[138] and several others show that iron consistently reduces ductility *and strength* of Al-7%Si-Mg alloys. This no doubt stems from the alloy in question having greater sensitivity to strength losses due to embrittlement than to the strengthening supplied by the iron.

The iron-manganese interaction is discussed opposite.

Manganese

Apart from very general statements regarding the action of manganese as an iron corrective, very little data exists regarding the effects of manganese additions. As was mentioned in Section 8.2.5, the iron-manganese interaction is very significant. However, within the iron limits imposed by BS1490-LM6 the beneficial effects of manganese addition are limited and the detrimental effects pronounced.

The effects of iron and manganese on tensile properties were illustrated in Figures 76,77, 78 and 79. As was shown, substantial differences exist regarding the effect of manganese depending on which modifier is used. When strontium is used, manganese greatly increases strength while having a minor detrimental effect on ductility. The gains in strength are supported by comments by Rooy[188], who states that manganese improves tensile properties. This comment was, however, directed at manganese additions to hypereutectic alloys. In contrast, when sodium is the major modifier, manganese additions cause only very slight strength gains and are again detrimental to ductility. In agreement, Mondolfo[78B] quotes several papers which conclude that when manganese is not used as an iron corrective it increases strength and reduces ductility.

In the presence of strontium and within the composition limits of BS1490-LM6, no evidence has been forthcoming to support the theory that manganese has the ability to reduce iron embrittlement. When sodium is used, reductions in iron embrittlement are evident and recommendations by Foseco that manganese additions be made at a rate governed by the following relationship have some foundation:

$$Mn\% = 2 \times (Fe\% - 0.5).$$

This function suggests that manganese need not be added if iron levels are below 0.5%, which is supported by the results given in Figure 78 since below this iron level, manganese has only detrimental effects on ductility. The Foseco function also indicates that a rapid increase in manganese level is required at iron levels beyond 0.5% which is also correct. However, within the LM6 range a more correct statement would be that manganese addition should only take place if:

$$Mn\% + Fe\% \geq 1.0$$

i.e. minimum iron and manganese levels exist for iron embrittlement to be effectively reduced.

The above comments do not take into account the effects of the iron/manganese interaction on properties such as proof and tensile strengths. As was mentioned in Section 8.2.5, the iron/manganese interaction does not have a significant effect on proof strength and hence this factor may be ignored. However, this interaction is influential on tensile strength. As shown in Figure 77, when strontium is used, tensile strength very rapidly decreases if Fe% + Mn% $\geq$ 0.85. If sodium is the modifier similar rapid tensile strength decreases occur when Fe% + Mn% $\geq$ 0.75. Given that these functions derive from empirical charts which incorporate experimental uncertainty they may not be regarded as precise, thus the general formula

$$Fe\% + Mn\% \geq 0.8$$

may be regarded as applicable irrespective of the modifier used. Mondolfo[78C] quotes this exact function as defining the composition at which $(FeMn)_3Si_2Al_{15}$ crystals become primary, therefore the formation of such crystals can be regarded as highly detrimental to tensile strength. The only complication regarding this finding is that, as mentioned in Section 8.3.2, microstructural analysis has suggested that in this study the FeMn phase becomes primary according to the following relationship:

$$1.25Mn\% + Fe\% \geq 0.6.$$

This leads to the conclusion that the primary FeMn phase is only present in sufficient volume to be influential when Fe% + Mn% $\geq$ 0.8, even though it initially forms when 1.25Fe% + Mn% $\geq$ 0.6. It is obvious from the loss of strength and reduced embrittlement expressions that manganese does not act as an iron embrittlement corrective without first causing substantial loss of strength. Kashyap et al[138] have published a plot of the effects of adding manganese to an Al-7%Si-Mg alloy of varying iron content. This alloy displays reduced strength due to manganese additions until iron levels exceed $\approx$ 0.45%. This is the reverse of the trends found with Al-12%Si and highlights how loss of ductility dominates the outcome of tensile strength tests of the lower silicon alloy.

Since manganese additions are referred to as hardeners, it is not surprising that manganese additions caused significant gains in this property. What is surprising is that the hardening influence does not vary depending on the modifier present. The lack of a manganese influence on modification was also largely expected, as most manganese and iron/manganese phases occur within primary aluminium dendrites and not in the eutectic

regions. Manganese additions were also found to increase porosity which may be an indication that the compacted-powder product used for manganese addition may have been a source of inclusions. As mentioned in Section 8.2.2, no sodium-modified manganese/porosity term was found, this is thought to have resulted from sodium-induced porosity masking the manganese effect. No evidence seems to exist explaining or supporting the possibility that manganese may only cause porosity in strontium containing alloys or acts as a source of hydrogen, thus these possibilities seem unlikely.

Finally, manganese has been found to be detrimental to grain refinement, which is what could be expected since it is obvious that the large manganese phases act as nuclei on which the aluminium dendrites form. Only one[49] reference could be found relating manganese to grain size and this simply referred to Russian work indicating that manganese has been shown to improve grain refinement. The only conceivable methods by which manganese phases could improve grain refinement are via multiple dendrite nucleation from each phase, or numerous individual manganese phase crystals may be present to act as individual nucleation sites. Given that the former does not seem to be the case in the microstructures observed here, without further information, the latter seems the only explanation for the Russian observation. This in turn implies that substantial manganese additions were made during the Russian experiments, i.e. > 1.0%.

9.4 GRAIN REFINERS (Titanium and Boron)

The interactions and effects relating to titanium and boron addition are exceedingly complex - important interactions occur between these elements and silicon, the modifiers and possibly phosphorus. As discussed in Section 2.3 and displayed in the results given in Section 8.2.4, the most pronounced and hence most researched effect of titanium and boron is grain refinement. Nevertheless, both titanium and boron have been shown to have very important effects on all of the other measured properties. Titanium- and boron-induced grain refinement effects are discussed separately below as they are particularly important and do not vary appreciably depending on the modifier used.

Boron

As illustrated in Section 8.2.1, in the presence of strontium, boron is highly detrimental to modification. Sigworth and Guzowski[64] note the detrimental influence boron has on strontium modification and suggest that this may be due to formation of a stable SrB_6 phase. This possibility is supported by the observation that sodium modification does not suffer similar detrimental effects due to boron. Information on the SrB_6 phase is scant at best. It is the only strontium-boron binary phase known to exist, yet little information is available regarding its formation and characteristics. Rooy[188] reports that boron has no influence on the eutectic coarseness of unmodified hypereutectic alloys, which supports the finding that boron does not directly coarsen the eutectic but rather impedes the action of strontium. It can be seen in Figure 48 that the deleterious effect that boron has on modification increases as silicon levels rise. This suggests that as eutectic volumes increase the degree of modifier interference also increases. As was shown in Section 2.7 (Figures 23 and 24) the influence of phosphorus increases markedly as silicon levels rise, thus if boron acts to liberate phosphorus from strontium (but not sodium) the observed modification characteristics displayed in Figure 48 would be expected.

The possibility of a significant strontium-boron interaction is further supported by the tensile strength, proof strength and ductility results. The effects of boron on each of these properties display significant variation depending on the presence of strontium. Although sodium-modified castings displayed no variation in eutectic refinement due to boron addition, notable detrimental boron effects on each of the tensile properties of these

castings were observed. In the case of sodium modification, decreased strength and ductility are assumed to be due to increased inclusion levels associated with the various boron additives. It is widely reported that boron additives are prone to causing problems due to introduction of associated inclusions[66, 67, 132B & 154B]. The increased porosity experienced with boron addition during this study would seem to confirm this problem. In the presence of strontium, the inclusion-induced effects are exacerbated much as would be expected given the increased eutectic coarseness. For example the modification and ductility variations attributed to boron display virtually identical forms (see Figures 48 and 89).

One notable observation amongst the tensile-test boron results is that the ductility variations between sodium and strontium modified samples decrease as the titanium level rises, i.e. 0.2% titanium appears to largely eliminate the boron-strontium interaction. This interaction has not been confirmed or contradicted by the remaining MLR data or other reports. The elimination of the strontium-boron interaction could result from titanium preventing the formation of SrB_6 or titanium off-setting the effects of liberated phosphorus. Some evidence exists supporting the latter theory as is mentioned below.

Titanium

As with boron addition, titanium-induced modification effects are more pronounced in the presence of strontium than sodium. Titanium has a beneficial effect on eutectic silicon refinement, something which has been discussed by authors such as Apelian and Cheng[187]. They show that titanium does not suppress eutectic solidification in the same way as conventional modifiers, rather it raises the eutectic temperature slightly irrespective of the presence of strontium. Zhang and Cantor[189] have shown that decreased aluminium purity increases eutectic silicon solidification temperatures, thus the ability of titanium to uniformly increase the eutectic temperature is exactly what would be expected from a "non-modifying" element. Ho and Cantor[190] have shown that changing the eutectic silicon solidification mode by the introduction of phosphorus does not influence the eutectic solidification temperature, thus the thermal cooling effects of titanium additions cannot be used to detect the presence of a titanium-phosphorus interaction. What can be concluded is that phosphorus does not affect primary and eutectic silicon solidification in exactly similar

ways. This supports comments by Gruzleski and Closset[18Y] that the mechanisms operating in the primary and eutectic crystallisation of silicon are probably quite different.

The above comments lead to the conclusion that the mechanism by which titanium modifies silicon is different, and independent from, conventional modification processes. Apelian and Cheng[187] conclude that "*Grain refining nucleants do not chemically modify the morphology of eutectic lamellae; these nucleants indirectly modify the eutectic. The structure in grain-refined castings which do not contain strontium is partially modified because of the physical restraints imposed on the transformation volume.*" If this was correct, boron would also act as a silicon refiner. As discussed above, this is not the case. The above authors support their theoretical refinement mechanism with micrographs of unrefined and titanium-refined castings which display unbranched, plate-like silicon of differing size with acicular silicon also present in the unrefined case. What is overlooked is that confined eutectic regions of the unrefined alloy do not display silicon plates of similar refinement as those occurring in the presence of titanium.

A possible explanation of the effects of titanium which would agree with the above boron findings is that titanium may neutralise the detrimental effects of phosphorus. Eliminating phosphorus would cause coarse acicular unmodified structures to be replaced by finer lamellar formations exactly as illustrated by Apelian and Cheng and indicated in Section 2.7, Figure 24. The possibility of titanium eliminating the effects of phosphorus was suggested by Loper and Sun[40] in 1989. These authors found that titanium counteracts the effects of deliberate phosphorus additions in hyper-eutectic alloys. This also supports the theory that the elimination of the boron/strontium interaction via titanium addition involves phosphorus neutralisation, as suggested above.

Titanium additions cause greater eutectic refinement in strontium modified samples than those modified with sodium. This could be a result of titanium countering the effects of boron in strontium modified samples and/or that the modification rating system used is based on qualitative factors rather than a truly quantitative scale. Titanium acts to substantially increase hardness; more so in the fine sodium-modified samples than the coarser strontium-modified structures. As would be expected, the addition of a hardening product with associated improvements in modification level translates into improved

strength. This effect is more pronounced in the presence of strontium than with sodium. Ductility is adversely effected by titanium addition however, this effect is moderated by the improved modification. As would be anticipated given the improved modification associated with strontium, titanium embrittlement is less severe in strontium modified samples. Since porosity levels did not vary with increased titanium additions, the reduced ductility is not thought to have originated from inadvertent simultaneous addition of inclusions.

The Titanium-Phosphorus-Boron Effect

The one plausible explanation of the titanium and boron effects shown above and mentioned by previous authors, has been alluded to above and may be summarised as:

A) Sodium and strontium eliminate the effects of phosphorus, possibly by dissolving the phosphorus in $NaSi_2$ and AlSiSr. Boron reacts with strontium, possibly forming SrB_6 which may effectively compromise strontium's ability to counteract phosphorus, hence boron indirectly coarsens the eutectic silicon. As would be expected given this mechanism, the detrimental effects of boron increase as silicon levels rise.

B) Titanium improves modification but does not interact with the modifying elements. Titanium does this by eliminating the detrimental effects of phosphorus, possibly by dissolving phosphorus within a solid solution of $TiSi_2$. This explanation is supported by the finding that titanium effectively eliminates the detrimental effects associated with combining boron and strontium.

The above process suggests a strong, indirect modification interaction between titanium and boron. Similarly, if titanium eliminates the strontium/boron interaction by forming $(Al,Ti)B_2$ in preference to SrB_6 a similar titanium/boron modification interaction should occur, yet no such function has been established via the MLR process.

Grain Refinement

Almost all of the published data surrounding the effects of titanium and boron addition concentrate solely on grain refinement, a topic which was covered in some detail in Section 2.3. Since titanium and boron are usually added in combination it was assumed that they would act in a synergistic fashion. However, as Figure 65 shows, this is not the case. What is also clear from the MLR results is that titanium and boron-induced grain refinement vary only slightly with sodium and strontium modification. This comes as somewhat of a surprise, given the results discussed above relating to the important interactions between boron, strontium and titanium. Evidently, the formation of SrB_6, should it occur, has only a minor influence on the grain refining ability of boron additives.

Complications arise when comparing Figure 65 and the results of work by other researchers, as most of the published results relating to the use of grain refining master alloys of differing composition quote alloy addition rates and not the actual cast composition. Addition rates are quoted as they provide direct information on how much of the various master alloys are required to achieve a specific degree of refinement. The various addition rates can then be readily converted into cost comparisons. Quoting master alloy addition rates makes no allowance for master alloys of nominally similar composition having different processing histories and thus varying effectiveness and recovery rates. The fact that titanium and boron recovery rates may vary widely depending on the master alloy composition has also largely been ignored. This means that using "addition rate" data as a basis for theoretical refinement mechanisms is seriously flawed due to a complete lack of knowledge regarding the actual cast composition. As an example of the variation in retention rates, in the present study boron retention varied from ≈60% for the 3% boron alloy to ≈100% for the 5%Ti - 1%B alloy. Titanium levels were found to have no influence on boron retention and vice versa. Thus master alloys have widely varying retention rates which may not be determined by master alloy compositions alone. The biggest drawback in not knowing the actual property variations as a function of cast composition is that changes in the pricing of titanium and boron cannot easily be converted into the production of the most effective and economical master alloy composition.

Figure 65 covers the Ti/B composition range permitted by BS1490-LM6, however commercial grain refiner levels are typically at the lower end of this range. The titanium levels in cast Al-7%Si-Mg alloys seldom exceed 0.1%, whilst in the Al-Si eutectic alloy typical levels are no more than 0.05%. Prior results by authors such as Vass[65] who conducted tests in a commercial environment, are further complicated since base alloys were used which contained appreciable titanium prior to the master alloy additions. Since almost all commercial castings contain less than 0.1%Ti and 0.012%B, this region of Figure 65 has been enlarged as the focus of Figure 97. It must be remembered when interpreting Figures 65 and 97 that the current testing was conducted on an alloy which initially contained ≈0.005%Ti and ≈0%B and although several final cast compositions contained less than 0.005%Ti the region adjacent to the boron axis is believed to be valid.

The refinement along the boron and titanium axes in Figure 97 suggests that AlB_{12} (or $AlB_2(?)$)* is a very potent grain refiner, more so than $TiAl_3$. It can also be seen that at titanium levels below ≈0.0775% the addition of boron and formation of the diboride $(Al,Ti)B_2$ is beneficial. It is also clear from the central region of the chart that boron in the form of the diboride $(Ti,Al)B_2$ is far less potent than AlB_{12} (or $AlB_2(?)$). Thus, titanium additions are not beneficial unless the retained titanium level is at least five times that of boron (see line $\overline{OA}$). This figure also shows that at titanium levels below 0.0775% boron addition is always beneficial but boron alone provides the greatest refinement if titanium levels do not exceed 25 times that of boron (see line $\overline{OB}$).

As mentioned in Section 2.3, Sigworth et al[64] and Vass[65] tested various Ti/B master alloys and each concluded that a 3%Ti-3%B master alloy produces more pronounced grain refinement than a 3% boron master alloy. These findings initially seem in complete contradiction to both the results presented above and those given by Lu et al[63] (presented in Section 2.3.3 as Figure 9). However, Vass actually started with a base alloy already containing appreciable titanium, thus the final titanium-boron ratios were to the right of the line $\overline{OA}$. As a result, additions of titanium and boron were more beneficial than similar additions of boron only, exactly as Figure 97 predicts. In agreement with this study, Vass also found that addition of ≥0.0775% titanium without boron promotes a finer grain size

* The actual amount of AlB_2 within the Al-3%B master alloy is still unknown.

than lower titanium levels in combination with boron. While Sigworth does not indicate the presence of prior titanium this is the only logical explanation for these findings.

Vass's[65] results show that in a commercial environment, equivalent additions of 6%Ti, 3%B and 3%Ti-3%B master alloys promote refinement for widely varying periods (see Figures 12 and 13). The 3%B alloy faded very rapidly, lasting only 15 minutes, while the 6%Ti alloy refined for 45-60 minutes. In comparison the 3%Ti-3%B alloy (which is a weaker refiner than the 6%Ti alloy) persisted for several hours. Whether the 3%B alloy would have faded as quickly in the absence of titanium is a question which remains to be answered.

Sigworth et al[64] report findings which suggest that AlB_{12} type boron alloys are totally ineffective grain refiners. This is in total disagreement with the findings of this research. This conclusion would not have been possible had the intended boron alloy been used. A possible explanation for this apparent anomaly is that AlB_{12} may be neutralised as a grain refiner by very rapid reaction with dissolved titanium. AlB_2 may react more slowly and hence not experience such rapid fade. This remains unsubstantiated but seems more likely than the boron alloy used in this study containing appreciable AlB_2.

Figures 65 and 97 represent the refinement results achieved after refiner contact periods of 5-6 minutes. The implications of longer melt holding periods should thus be considered. It is well established that titanium fades rapidly while titanium/boron combinations are far more resilient (- the whole point of their development). Subject to the initial titanium content (as discussed above) boron as a sole refiner fades even faster than titanium. Given these findings it can be expected that the refinement characteristics indicated in Figure 97 would vary with time in the manner indicated. Refiner fade will also be influenced by turbulence (possibly from periodic degassing). If this is sufficient to maintain the boride particles in suspension, boron fade can be expected to be minimal. The changes that may occur to Figure 97 with melt holding time indicate that in commercial situations where such periods are prolonged, the composition "window" in which combined titanium and boron additions are the most effective option rapidly expands.

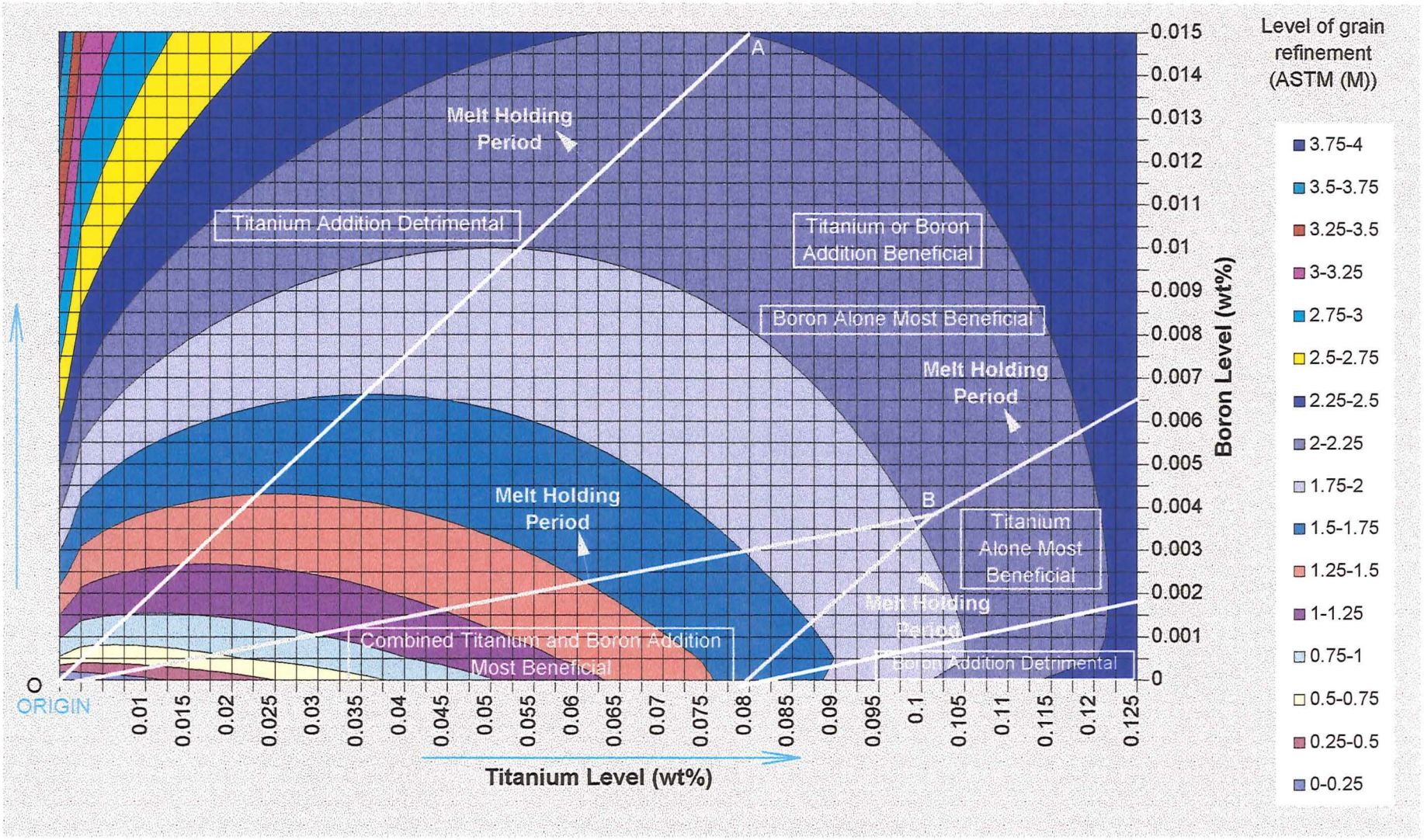


Figure 97: The influence of lower levels of titanium and boron on the grain-refinement of Al-Si eutectic alloys.

Titanium and boron have exceedingly complex and very poorly understood effects on the properties of aluminium castings. As discussed above, boron is associated with a number of detrimental effects, particularly in the presence of strontium, and these effects appear to occur irrespective of the boron master alloy used. These effects must be carefully weighed against the benefits of increased resistance to refinement fade. Given the above results it would seem prudent to moderate the use of boron-containing master alloys wherever possible.

9.5 OTHER FINDINGS AND COMPLICATIONS

The Compositional Variations Used

The reasons and logic behind the sample compositions encountered in this research were detailed in Chapters Three and Five. In retrospect, certain of the elements investigated have not displayed the variability in recovery rate initially anticipated. Iron, manganese and magnesium were all added with an accuracy which was greater than originally expected. This has meant that interactions such as that between iron and manganese have fewer "non-aim" compositions than would ideally have been desired. Future founders and researchers should take this into account when using the results provided in this report.

Copper and Other Secondary Variables

As was noted in Section 8.2.2, the copper content was found to be an influential factor in the prediction of porosity levels. This was the only element outside of the main variable set which proved significant in the MLR process. Not all of the measured elements were included as variables in all of the MLR analyses performed, thus it is possible that significant factors for which composition data is already available have been overlooked. The parameters most likely to yield improved predictive ability via more complete composition analysis are hardness and proof strength. The proof strength of as-cast structures is normally considered to be a function of composition alone. The fine surface finish used on the tensile test pieces and the careful manner in which the tensile testing was performed, suggest that factors other than composition should not be significant in proof strength variation. From the above discussion, it can be surmised that the low predictive

worth of the MLR proof strength results is an indication of the complexity of the interactions taking place between elements.

Boron and Phosphorus

The use of a different boron additive to that intended and the inability to analyse for phosphorus were factors that were expected to impose major limitations on the accuracy and application of the MLR results presented in this thesis. As the results throughout Chapter 8 illustrate, these compromises have not been as significant as anticipated and have not prevented numerous findings being reached.

As was shown in Figures 65 and 91, the 3%B AlB_{12} master alloy did not cause significantly different variations in tensile strength or grain refinement compared with the 5%Ti-1%B master alloy. This suggests that future investigators or founders employing master alloys of the AlB_2 type should be able to use the results reported here without experiencing variability other than that suggested by the correlation coefficients and the error values given in Appendix O.

The significance of phosphorus variation when relating the results from this study to other situations is difficult to assess. As was shown in Section 8.1 (Figure 45), modification variation between the samples subject to deliberate CuP addition and the remaining samples was less than the variability inherent in the modification measurement and MLR analysis. This may well be due to minimal phosphorus retention, however it was expected that phosphorus levels would rise by at least 2-3 ppm. If phosphorus levels did vary by 2-3 ppm it could be concluded that the quantified results of this study should apply directly to any virgin alloy. Since this cannot be confirmed, it is suggested that use of the results given herein be treated with due regard for potential complications due to phosphorus variation.

10.0 CONCLUSIONS

The production and analysis of 495 sand-cast Al-Si eutectic samples, each of a different composition within the BS1490-LM6 range, has enabled the individual and combined structural and physical effects of variations in Na, Sr, Ti, B, Si, Mg, Mn and Fe levels to be quantified. The results which have stemmed from extensive multi-linear-regression analysis can be used to forecast cast characteristics such as: hardness, the tensile properties, eutectic silicon morphology, propensity to form porosity, and grain size for virtually any commercial Al-Si eutectic alloy which may be encountered. The final results, which are presented in Chapter 8, are of a form which may be interpreted by people without a rigorous technical background or familiarity with the subtleties of Al-Si eutectic casting. A factor which must be taken into account when using the results presented in Chapter 8 is that the small scale melts used in this research almost certainly contained higher inclusion levels than would be encountered commercially. The implications of this are that the recorded (and hence predicted) tensile strength and ductility values will most likely be lower than those encountered in a commercial environment. Similarly, the predicted porosity levels will likely be higher than those produced. A further issue, which should not be overlooked, is that due to the lack of a suitable compositional analysis method, it has been impossible to account for the effects of phosphorus variation.

While the statistical analysis results have provided answers to several contentious issues, they have also provided insights into several areas deserving further investigation. In addition to the final results presented in Chapter 8, the most significant conclusions derived from analysis of the final cast specimen properties may be summarised as:

- Contrary to some reports[138], silicon variation within the range of interest (9.5-13.5%Si) has significant effects on cast grain size and mechanical properties. Optimal tensile properties are encountered with silicon levels in the range 11.3-12.5% while grain refinement is most pronounced in the actual eutectic region from 12.5-13.5%Si.

Interestingly, silicon consistently increases hardness yet the form the silicon assumes (i.e. modification level) is of minimal significance.

- The two conventional modifiers investigated have distinctly different characteristics, for example: sodium aids grain refinement while strontium has a slight coarsening effect; sodium induces significant porosity increases while strontium does not; sodium addition can induce strength and ductility increases of more than twice those attainable with strontium; and finally, the most favourable modification state achieved with sodium is quite distinct and well defined, while that associated with optimum strontium is not. This last point makes metallographic determination of the optimal strontium modification state very difficult.

- In the absence of modification, magnesium has beneficial strengthening effects. Magnesium in combination with the modifiers produces coarse eutectic banding which not only lowers the modification rating but reduces strength and ductility. Magnesium-related coarsening cannot be eliminated by increased modifier addition. However, beneficial modification effects are never completely overcome even with magnesium levels at the upper limit imposed by BS1490-LM6. Magnesium is also found to increase hardness and porosity levels but has no detectable effect on grain refinement.

- The effects of iron and manganese are closely inter-related with both the hardness and tensile properties displaying very significant interactions. Both iron and manganese significantly increase hardness, however these effects are moderated as the combined iron and manganese levels rise. Irrespective of the modifier used, when combined iron and manganese levels exceed 0.8%, the pronounced strengthening effect of iron is rapidly eliminated. In agreement with numerous findings, iron was found to be detrimental to ductility. This effect in itself is not considered significant enough to warrant undue concern, particularly when virgin alloys are processed. The ability of manganese to reduce iron embrittlement was also confirmed, however this effect was minimal within the confines of the given composition range. Gains in ductility experienced at high combined iron and manganese levels (Fe% +Mn% $\geq$ 1.0) are outweighed by the associated tensile strength losses, hence deliberate additions of manganese would appear to have little or no merit.

- Similarly to iron and manganese, the effects of titanium and boron are inter-related in several of the properties monitored. These grain refiners were not found to act in a synergistic manner. Rather, at conventional addition levels, the addition of boron alone caused more refinement than a similar addition in conjunction with titanium. Titanium had a strong hardening effect which at low titanium levels was increased and at high titanium levels decreased by the presence of boron. Titanium, which was found to act as a weak modifier (particularly in the presence of strontium), caused significant strength increases and slight decreases in ductility. Conversely, boron was extremely detrimental to modification and all of the tensile properties even when added in very minor amounts. Boron was also attributed with causing significantly increased porosity. Clearly, boron-containing products required to delay grain refiner fade should not be added at levels any higher than those absolutely necessary.

- It appears that titanium has the ability to eliminate the effects of phosphorus. In strontium-modified structures, boron has the opposite effect to titanium i.e. phosphorus neutralisation by strontium seems to be severely compromised by the presence of boron. Similar modifier interference was not detected in the presence of sodium hence the effects of boron are not as detrimental in sodium-modified structures.

The combined statistical analysis results may be generalised to give the following findings:

- Alloys containing low levels of iron, silicon, boron and magnesium ($\approx$<0.3%, <11%, <0.005% and <0.03% respectively), experience difficulty meeting the tensile strength requirements of BS1490-LM6. This problem may be eliminated by careful eutectic silicon modification via the addition of 0.01-0.015% sodium.

- Conversely, ductility tends to be the critical factor controlling whether alloys containing high levels of iron, silicon, boron and magnesium consistently surpass the specified physical requirements of BS1490-LM6. Only in the most contaminated alloys is the increase in ductility associated with sodium modification insufficient to counteract the combined detrimental effects of these elements.

- It is clear that due to the inherent variability associated with sodium modification and the sand-casting process, certain composition permutations within the investigated composition range will not consistently meet the physical requirements of BS1490-LM6 irrespective of the care taken during molten processing and final casting.

- Taking all casting characteristics into account, the optimum composition combination would appear to be ≈0.012%Na, 11.5%Si, 0%Mg, >0.3%Fe, 0%Mn with as much Ti and as little B as feasible whilst still achieving the grain refinement necessary to produce the casting soundness and surface finish necessary.

During the course of producing the cast specimens, investigations were carried out into the suitability of various materials in the role of fluxing gas lances. The compositional variation and contamination which occurs during conventional lance or tablet degassing was also monitored. The full results of this experimental work were presented in Chapter 4, however the main conclusions are:

Degassing Lance Material Experiments

- Degassing lances constructed in low carbon and austenitic stainless steel experienced rapid degradation when exposed to molten aluminium. The level of contamination and rapid degradation experienced with these materials confirmed their unsuitability for exposure to molten aluminium.

- The application of a purpose-designed commercial refractory paste to steel tools and lances reduced degradation and contamination appreciably.

- Melt contamination was negligible when graphite or ceramic degassing lances were employed. A ceramic lance constructed of SL60ZA alumina type ceramic suffered from a lack of thermal shock resistance so negating further use of this material. No financially viable alternative ceramic was located, hence all later sample production was conducted using a graphite lance which proved adequate.

Composition Variation Due to Degassing

- Sodium losses during degassing were extremely rapid and exponential in nature irrespective of the fluxing gas used. Conversely, strontium losses were slight, supporting the feasibility of producing strontium-premodified foundry ingot.

- While the formation of NaCl is thermodynamically more favourable than $MgCl_2$, sodium does not sacrificially protect magnesium in melts exposed to chlorine. In such cases the presence of sodium actually expedites magnesium removal. Clearly a sodium/magnesium interaction exists which has previously not been fully appreciated .

- Depletion of titanium and boron is appreciable irrespective of the modifier or degassing medium used.

- Silicon levels dropped more quickly in the presence of sodium than in its absence. Evidence exists to suggest that this trend is a result of optical-emission-spectrometer inaccuracy due to a silicon/sodium interaction rather than actual silicon loss.

A more complete summary of the conclusions drawn from the composition variation during degassing experiments may be found in Section 4.3.

In summary, the major achievement of this research has been to provide a series of statistically significant expressions relating the physical and structural properties of sand-cast aluminium-silicon eutectic alloy to most of the compositional variations encountered by commercial foundries. This research has also provided a foundation of quantified results which highlight numerous issues in need of further investigation and constitute a database upon which future experimental design may draw. Data has also been produced relating degassing tools and mechanisms to melt composition variation.

11.0 RECOMMENDATIONS FOR FUTURE INVESTIGATION

The time and effort required to produce more than a few castings of varying composition is often a major limitation when considering research proposals. Due to the numerous significant casting and alloy variations which arise during foundry research, the information required for optimised experimental design is often not available, thus exacerbating limitations imposed on the composition ranges investigated. Samples of each of the 495 different Al-Si eutectic alloys cast during the course of the current research have been retained, thus the opportunity exists to utilise these specimens in future research which may not otherwise be viable. The retained specimens consist of test-bar shrinkage-heads (≈500g) and metallographically-polished cross-section discs. Of the various future investigation possibilities listed below, the most significant would appear to be the incorporation of phosphorus analysis into the sample data already recorded. Hence, the existing samples should be used with due thought and consideration.

An issue which was discussed in Section 8.3.2 but which is not covered below is the development of non-equilibrium phase diagrams representative of the sand-cast test-bar solidification conditions used worldwide. The development of such diagrams with the required accuracy would involve extensive metallographic and analytical analysis. At present, such a project may seem unrealistic, but if the current advances made in image analysis capabilities and availability continue, it may soon be within the bounds of practicality.

11.1 FUTURE INVESTIGATION UTILISING THE ALLOYS PRODUCED

(a) Phosphorus Analysis

Phosphorus analysis has been dealt with in some detail in Section 3.3. If phosphorus levels could be assessed in the cast specimens the resulting property variations could be quantified by the multi-linear-regression process. Should phosphorus variation prove as significant as anticipated, a large proportion of the

variability in the current statistical analysis results could be removed, thus improving the stated prediction significance values.

It would appear that wet chemical means are the only methods by which phosphorus analysis may be performed to the required accuracy of ±1ppm. While the wet analysis by NZAS staff has proved unsuccessful, this is thought to have been caused by composition variability which could not be accounted for in the standards available. Any future analysis attempts must first establish the chosen analysis method and then counteract the masking and interference effects due to the wide compositional variation required. The latter is unlikely to be achieved without a very sound initial experimental design and possible production of further cast specimens.

(b) Thermal and Resistivity Analysis

While some controversy persists regarding the issue of microstructural assessment by thermal analysis, the information provided by authors such as Closset, Gruzleski, Apelian, etc[(see 18Z)] is largely in agreement when it is viewed in its true context.

As mentioned in Sections 2.2 and 2.3, both grain refinement and modification may be assessed by thermal analysis techniques. The former is indicated by little or no apparent supercooling while the latter is measured by the eutectic temperature, the degree of eutectic nucleation undercooling and the undercooling period. Each of these factors could be measured in the pre-existing alloys by employing conventional thermal analysis techniques. Provided that the existing sample metal is rapidly melted and not held in a molten state for protracted periods it is doubtful that composition variation would be significant and hence the current composition data could be employed. The results of such work would not only illustrate the effects of impurity elements on grain refinement and modification measurement but also allow derivation of functions relating composition to exact eutectic temperature and shift, i.e. silicon equivalence. An expression of this type relating Al-Si sample composition to eutectic temperature has already been produced by Mondolfo[(see 18Z)].

$$\text{Eutectic Temp (°C)} = 577 - 12.5\%\text{Si}[4.43\%\text{Mg} + 1.43\%\text{Fe} + 1.93\%\text{Cu} + 1.7\%\text{Zn} + 3.0\%\text{Mn} + 4.0\%\text{Ni}]$$

This equation only applies to unmodified alloys with less than 1% of elements other than aluminium and silicon; analysing the pre-existing specimens would allow both verification and expansion of this expression.

In addition to thermal analysis, resistivity analysis has been the subject of several relatively recent studies regarding rapid microstructural analysis. Resistivity testing of cast specimens is rapid and simple without the requirement for excessively expensive or complicated equipment. While the results of resistivity testing are unlikely to prove as informative as those derived from thermal analysis, the effects of various impurity elements could undoubtedly be established.

(c) Corrosion, Impact, Shrinkage and Wear Testing

Measurements of the effects of compositional variations on corrosion, shrinkage, wear and impact properties would necessitate production of coupons cast to the required form. Provided the coupon production was conducted in the appropriate manner, production of fresh alloys would not be necessary to maintain the relevance of the current composition data. Any recasting would have to be performed by a reasonably rapid melting and recasting process* . To minimise variability and maximise the significance of any of these tests, it is recommended that the molten metal be filtered during any future coupon production processes. It would also be advantageous to equalise the sample gas levels, however, achieving this without causing significant compositional changes may prove difficult. Without equalised or very low gas levels it is difficult to envisage shrinkage tests, such as Tatur tests, providing meaningful results. It is possible that following rapid processing retained hydrogen levels will be consistent and low; this would, however, require substantiating.

The fundamental issue of the relevance of carrying out impact tests on predominantly face-centred-cubic structures such as aluminium castings, needs to be resolved. Impact testing is simply a measure of fracture resistance or the energy absorbed during fracture. This energy can also be found by integrating the area

* Due to variations in cooling rate, the *physical* and *structural* property data recorded in the present research, would not apply to future coupons which may be produced.

under a stress strain curve. Impact testing is a relatively imprecise procedure compared to tensile testing, thus depending on the characteristics of the material being tested and the accuracy of the required results, impact testing is not always appropriate. Speed and ease are the only advantages gained by impact-testing metals which do not undergo changes in fracture mechanism depending on the test speed or temperature. Since no data is readily available suggesting that aluminium-silicon structures undergo significant variations in fracture mechanism depending on fracture speed or temperature there seems little reason, other than ease, for impact testing such structures.

Authors increasingly quote impact test results for aluminium castings, hence two issues need to be addressed: firstly, does a transition in fracture mechanism occur which can be highlighted by impact testing, and secondly, are the impact test procedures currently being used suitable for highlighting any variations in fracture mechanism which may occur?

11.2 FUTURE INVESTIGATIONS REQUIRING FURTHER ALLOY PRODUCTION

(a) Potential Interaction Confirmation

As mentioned in Chapter 8 potentially significant Mg-Na/Sr-P, Ti-P, B-P-Sr-Ti interactions have been postulated to explain the MLR results. As conclusive investigation into each of these reactions necessitates phosphorus analysis, they are not expected to be easily confirmed without careful prior experimental design, sample production and chemical analysis.

(b) Fatigue Testing

Scant information appears to exist on the effects of impurities on the fatigue properties of Al-Si eutectic alloys. Some information is available regarding the effect of magnesium, see Section 2.6, but not other elements. A real need exists for more publicly available information on this important subject. It is possible that iron is detrimental to fatigue strength as this potentially significant effect is

suggested by authors such as Wickburg et al[113]. While the findings presented by Wickburg have been quoted by later authors[138], the original data appears far from conclusive and only concerns the Al-7%Si-Mg alloy. The effects of the modifiers and grain refiners on fatigue also need investigation. Due to the associated introduction of inclusions, boron additives will almost certainly have detrimental effects on fatigue life, their effects are thus particularly deserving of investigation.

The various alloy samples which exist from the current research are not substantial enough to create specimens of the size which would be required for acceptable fatigue tests, hence it is unlikely that future research will be able to utilise samples from this study.

(c) Standard Test Bar Filtration

As mentioned in Section 2.5, extensive effort has been expended in recent years on providing and studying the implications of increasingly cleaner metal. As discussed, the removal of inclusions from cast metal substantially improves casting properties such as tensile strength, ductility, fluidity, surface finish and machinability. The most widely adopted method of cleaning molten metal is the incorporation of ceramic filters into mould gates and runners, thus large quantities of castings are now produced from metal which is filtered within the mould. Interestingly, the metal used in standard test bars, by which these same castings are judged, is not filtered in a similar manner. As no standards specify the need for modification, let alone filtration, there seems to be no reason why in-mould filtration should invalidate test bar results.

It would be of interest to know if the use of well-designed test-bar feeders which incorporate filters could significantly reduce the number of commercial test bars which fail to achieve the necessary mechanical properties. While using filters in this way may seem like "cheating", the test bars produced would often be more representative of the cast metal than is currently the case.

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Appendix A
British Standard 1490-LM6

Composition and Physical Property Limits

Designation	LM6	
Nominal Composition	Al-Si12	
Aluminium Association Alloy	A413.2	
European Alloy	AlSi12	
Australian Standard	__401, e.g. CA, BB, etc	
Other	160 series	
Nearest Alloys in ISO 3522	Al-Si12 Al-Si12Fe	
Elements	**Minimum %**	**Maximum %**
Aluminium	Remainder	
Cooper	-	0.1
Magnesium	-	0.10
Silicon	10.0	13.0
Iron	-	0.6
Manganese	-	0.5
Nickel	-	0.1
Zinc	-	0.1
Lead	-	0.1
Tin	-	0.05
Titanium	-	0.2
Each Other Element*	-	0.05
Total Other Element*	-	0.15

* Modifiers not included

In an "as cast" condition LM6 must meet the following mechanical property criteria:-

Tensile Strength:

Sand or investment cast	160 N/mm^2 (minimim)
Chill cast	190 N/mm^2 (minimim)

Elongation on $5.65\sqrt{S_o}$ ***:**

Sand or investment cast	5% (minimim)
Chill cast	7% (minimim)

* S_o = Original cross-sectional area of the parallel length.

Appendix B

Final Aim Composition Listing -the experiment design

-The initial sample layout may be found by ignoring the titanium column and including the phosphorus in samples 1-204.

-The final sample composition aims did not contain phosphorus so the end column may be ignored.

Composition	Silicon	Sodium	Strontium	Magnesium	Manganese	Iron	Titanium	Boron	*Phosphorus*
#	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	*ppm*
Group One									
1	10	0.015	0	min.	min.	min.	min.	min.	min.
2	10	0.015	0	min.	min.	0.6	min.	min.	min.
3	10	0.015	0	min.	0.2	min.	min.	min.	min.
4	10	0.015	0	min.	0.2	0.6	min.	min.	min.
5	10	0.015	0	min.	0.5	min.	min.	min.	min.
6	10	0.015	0	min.	0.5	0.6	min.	min.	min.
7	10	0.015	0	0.1	min.	min.	min.	min.	min.
8	10	0.015	0	0.1	min.	0.6	min.	min.	min.
9	10	0.015	0	0.1	0.2	min.	min.	min.	min.
10	10	0.015	0	0.1	0.2	0.6	min.	min.	min.
11	10	0.015	0	0.1	0.5	min.	min.	min.	min.
12	10	0.015	0	0.1	0.5	0.6	min.	min.	min.
13	10	0.015	0	min.	min.	min.	0.1	min.	6
14	10	0.015	0	min.	min.	0.6	0.1	min.	6
15	10	0.015	0	min.	0.2	min.	0.1	min.	6
16	10	0.015	0	min.	0.2	0.6	0.1	min.	6
17	10	0.015	0	min.	0.5	min.	0.1	min.	6
18	10	0.015	0	min.	0.5	0.6	0.1	min.	6
19	10	0.015	0	0.1	min.	min.	0.1	min.	6
20	10	0.015	0	0.1	min.	0.6	0.1	min.	6
21	10	0.015	0	0.1	0.2	min.	0.1	min.	6
22	10	0.015	0	0.1	0.2	0.6	0.1	min.	6
23	10	0.015	0	0.1	0.5	min.	0.1	min.	6
24	10	0.015	0	0.1	0.5	0.6	0.1	min.	6
25	10	0.015	0	min.	min.	min.	0.2	min.	11
26	10	0.015	0	min.	min.	0.6	0.2	min.	11
27	10	0.015	0	min.	0.2	min.	0.2	min.	11
28	10	0.015	0	min.	0.2	0.6	0.2	min.	11
29	10	0.015	0	min.	0.5	min.	0.2	min.	11
30	10	0.015	0	min.	0.5	0.6	0.2	min.	11
31	10	0.015	0	0.1	min.	min.	0.2	min.	11
32	10	0.015	0	0.1	min.	0.6	0.2	min.	11
33	10	0.015	0	0.1	0.2	min.	0.2	min.	11
34	10	0.015	0	0.1	0.2	0.6	0.2	min.	11
35	10	0.015	0	0.1	0.5	min.	0.2	min.	11
36	10	0.015	0	0.1	0.5	0.6	0.2	min.	11
37	10	0	0.025	min.	min.	min.	min.	min.	min.
38	10	0	0.025	min.	min.	0.6	min.	min.	min.
39	10	0	0.025	min.	0.2	min.	min.	min.	min.
40	10	0	0.025	min.	0.2	0.6	min.	min.	min.
41	10	0	0.025	min.	0.5	min.	min.	min.	min.
42	10	0	0.025	min.	0.5	0.6	min.	min.	min.
43	10	0	0.025	0.1	min.	min.	min.	min.	min.
44	10	0	0.025	0.1	min.	0.6	min.	min.	min.
45	10	0	0.025	0.1	0.2	min.	min.	min.	min.
46	10	0	0.025	0.1	0.2	0.6	min.	min.	min.
47	10	0	0.025	0.1	0.5	min.	min.	min.	min.
48	10	0	0.025	0.1	0.5	0.6	min.	min.	min.
49	10	0	0.025	min.	min.	min.	0.1	min.	6
50	10	0	0.025	min.	min.	0.6	0.1	min.	6
51	10	0	0.025	min.	0.2	min.	0.1	min.	6
52	10	0	0.025	min.	0.2	0.6	0.1	min.	6
53	10	0	0.025	min.	0.5	min.	0.1	min.	6
54	10	0	0.025	min.	0.5	0.6	0.1	min.	6
55	10	0	0.025	0.1	min.	min.	0.1	min.	6

Composition	Silicon	Sodium	Strontium	Magnesium	Manganese	Iron	Titanium	Boron	*Phosphorus*
#	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	*ppm*
56	10	0	0.025	0.1	min.	0.6	0.1	min.	6
57	10	0	0.025	0.1	0.2	min.	0.1	min.	6
58	10	0	0.025	0.1	0.2	0.6	0.1	min.	6
59	10	0	0.025	0.1	0.5	min.	0.1	min.	6
60	10	0	0.025	0.1	0.5	0.6	0.1	min.	6
61	10	0	0.025	min.	min.	min.	0.2	min.	11
62	10	0	0.025	min.	min.	0.6	0.2	min.	11
63	10	0	0.025	min.	0.2	min.	0.2	min.	11
64	10	0	0.025	min.	0.2	0.6	0.2	min.	11
65	10	0	0.025	min.	0.5	min.	0.2	min.	11
66	10	0	0.025	min.	0.5	0.6	0.2	min.	11
67	10	0	0.025	0.1	min.	min.	0.2	min.	11
68	10	0	0.025	0.1	min.	0.6	0.2	min.	11
69	10	0	0.025	0.1	0.2	min.	0.2	min.	11
70	10	0	0.025	0.1	0.2	0.6	0.2	min.	11
71	10	0	0.025	0.1	0.5	min.	0.2	min.	11
72	10	0	0.025	0.1	0.5	0.6	0.2	min.	11
73	13	0.015	0	min.	min.	min.	min.	min.	min.
74	13	0.015	0	min.	min.	0.6	min.	min.	min.
75	13	0.015	0	min.	0.2	min.	min.	min.	min.
76	13	0.015	0	min.	0.2	0.6	min.	min.	min.
77	13	0.015	0	min.	0.5	min.	min.	min.	min.
78	13	0.015	0	min.	0.5	0.6	min.	min.	min.
79	13	0.015	0	0.1	min.	min.	min.	min.	min.
80	13	0.015	0	0.1	min.	0.6	min.	min.	min.
81	13	0.015	0	0.1	0.2	min.	min.	min.	min.
82	13	0.015	0	0.1	0.2	0.6	min.	min.	min.
83	13	0.015	0	0.1	0.5	min.	min.	min.	min.
84	13	0.015	0	0.1	0.5	0.6	min.	min.	min.
85	13	0.015	0	min.	min.	min.	0.1	min.	6
86	13	0.015	0	min.	min.	0.6	0.1	min.	6
87	13	0.015	0	min.	0.2	min.	0.1	min.	6
88	13	0.015	0	min.	0.2	0.6	0.1	min.	6
89	13	0.015	0	min.	0.5	min.	0.1	min.	6
90	13	0.015	0	min.	0.5	0.6	0.1	min.	6
91	13	0.015	0	0.1	min.	min.	0.1	min.	6
92	13	0.015	0	0.1	min.	0.6	0.1	min.	6
93	13	0.015	0	0.1	0.2	min.	0.1	min.	6
94	13	0.015	0	0.1	0.2	0.6	0.1	min.	6
95	13	0.015	0	0.1	0.5	min.	0.1	min.	6
96	13	0.015	0	0.1	0.5	0.6	0.1	min.	6
97	13	0.015	0	min.	min.	min.	0.2	min.	11
98	13	0.015	0	min.	min.	0.6	0.2	min.	11
99	13	0.015	0	min.	0.2	min.	0.2	min.	11
100	13	0.015	0	min.	0.2	0.6	0.2	min.	11
101	13	0.015	0	min.	0.5	min.	0.2	min.	11
102	13	0.015	0	min.	0.5	0.6	0.2	min.	11
103	13	0.015	0	0.1	min.	min.	0.2	min.	11
104	13	0.015	0	0.1	min.	0.6	0.2	min.	11
105	13	0.015	0	0.1	0.2	min.	0.2	min.	11
106	13	0.015	0	0.1	0.2	0.6	0.2	min.	11
107	13	0.015	0	0.1	0.5	min.	0.2	min.	11
108	13	0.015	0	0.1	0.5	0.6	0.2	min.	11
109	13	0	0.025	min.	min.	min.	min.	min.	min.
110	13	0	0.025	min.	min.	0.6	min.	min.	min.
111	13	0	0.025	min.	0.2	min.	min.	min.	min.
112	13	0	0.025	min.	0.2	0.6	min.	min.	min.
113	13	0	0.025	min.	0.5	min.	min.	min.	min.
114	13	0	0.025	min.	0.5	0.6	min.	min.	min.
115	13	0	0.025	0.1	min.	min.	min.	min.	min.
116	13	0	0.025	0.1	min.	0.6	min.	min.	min.
117	13	0	0.025	0.1	0.2	min.	min.	min.	min.
118	13	0	0.025	0.1	0.2	0.6	min.	min.	min.
119	13	0	0.025	0.1	0.5	min.	min.	min.	min.
120	13	0	0.025	0.1	0.5	0.6	min.	min.	min.
121	13	0	0.025	min.	min.	min.	0.1	min.	6
122	13	0	0.025	min.	min.	0.6	0.1	min.	6

Composition	Silicon	Sodium	Strontium	Magnesium	Manganese	Iron	Titanium	Boron	*Phosphorus*
#	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	*ppm*
123	13	0	0.025	min.	0.2	min.	0.1	min.	6
124	13	0	0.025	min.	0.2	0.6	0.1	min.	6
125	13	0	0.025	min.	0.5	min.	0.1	min.	6
126	13	0	0.025	min.	0.5	0.6	0.1	min.	6
127	13	0	0.025	0.1	min.	min.	0.1	min.	6
128	13	0	0.025	0.1	min.	0.6	0.1	min.	6
129	13	0	0.025	0.1	0.2	min.	0.1	min.	6
130	13	0	0.025	0.1	0.2	0.6	0.1	min.	6
131	13	0	0.025	0.1	0.5	min.	0.1	min.	6
132	13	0	0.025	0.1	0.5	0.6	0.1	min.	6
133	13	0	0.025	min.	min.	min.	0.2	min.	11
134	13	0	0.025	min.	min.	0.6	0.2	min.	11
135	13	0	0.025	min.	0.2	min.	0.2	min.	11
136	13	0	0.025	min.	0.2	0.6	0.2	min.	11
137	13	0	0.025	min.	0.5	min.	0.2	min.	11
138	13	0	0.025	min.	0.5	0.6	0.2	min.	11
139	13	0	0.025	0.1	min.	min.	0.2	min.	11
140	13	0	0.025	0.1	min.	0.6	0.2	min.	11
141	13	0	0.025	0.1	0.2	min.	0.2	min.	11
142	13	0	0.025	0.1	0.2	0.6	0.2	min.	11
143	13	0	0.025	0.1	0.5	min.	0.2	min.	11
144	13	0	0.025	0.1	0.5	0.6	0.2	min.	11
Group Two									
145	11.5	0.015	0	min.	0.2	min.	min.	min.	min.
146	11.5	0.015	0	min.	0.2	0.6	min.	min.	min.
147	11.5	0.015	0	0.1	0.2	min.	min.	min.	min.
148	11.5	0.015	0	0.1	0.2	0.6	min.	min.	min.
149	11.5	0.015	0	min.	0.2	min.	0.1	min.	6
150	11.5	0.015	0	min.	0.2	0.6	0.1	min.	6
151	11.5	0.015	0	0.1	0.2	min.	0.1	min.	6
152	11.5	0.015	0	0.1	0.2	0.6	0.1	min.	6
153	11.5	0.015	0	min.	0.2	min.	0.2	min.	11
154	11.5	0.015	0	min.	0.2	0.6	0.2	min.	11
155	11.5	0.015	0	0.1	0.2	min.	0.2	min.	11
156	11.5	0.015	0	0.1	0.2	0.6	0.2	min.	11
157	11.5	0	0.025	min.	0.2	min.	min.	min.	min.
158	11.5	0	0.025	min.	0.2	0.6	min.	min.	min.
159	11.5	0	0.025	0.1	0.2	min.	min.	min.	min.
160	11.5	0	0.025	0.1	0.2	0.6	min.	min.	min.
161	11.5	0	0.025	min.	0.2	min.	0.1	min.	6
162	11.5	0	0.025	min.	0.2	0.6	0.1	min.	6
163	11.5	0	0.025	0.1	0.2	min.	0.1	min.	6
164	11.5	0	0.025	0.1	0.2	0.6	0.1	min.	6
165	11.5	0	0.025	min.	0.2	min.	0.2	min.	11
166	11.5	0	0.025	min.	0.2	0.6	0.2	min.	11
167	11.5	0	0.025	0.1	0.2	min.	0.2	min.	11
168	11.5	0	0.025	0.1	0.2	0.6	0.2	min.	11
Group Three (i)									
169	11.5	0	0	min.	min.	min.	min.	min.	min.
170	11.5	0.005	0	min.	min.	min.	min.	min.	min.
171	11.5	0.01	0	min.	min.	min.	min.	min.	min.
172	11.5	0.015	0	min.	min.	min.	min.	min.	min.
173	11.5	0.02	0	min.	min.	min.	min.	min.	min.
174	11.5	0.03	0	min.	min.	min.	min.	min.	min.
175	11.5	0.04	0	min.	min.	min.	min.	min.	min.
176	11.5	0.05	0	min.	min.	min.	min.	min.	min.
177	11.5	0	0.005	min.	min.	min.	min.	min.	min.
178	11.5	0	0.01	min.	min.	min.	min.	min.	min.
179	11.5	0	0.02	min.	min.	min.	min.	min.	min.
180	11.5	0	0.025	min.	min.	min.	min.	min.	min.
181	11.5	0	0.03	min.	min.	min.	min.	min.	min.
182	11.5	0	0.04	min.	min.	min.	min.	min.	min.
183	11.5	0	0.05	min.	min.	min.	min.	min.	min.
Group Three (ii)									
184	11.5	0	0	0.1	0.5	0.6	0.2	min.	11
185	11.5	0.005	0	0.1	0.5	0.6	0.2	min.	11
186	11.5	0.01	0	0.1	0.5	0.6	0.2	min.	11

Composition	Silicon	Sodium	Strontium	Magnesium	Manganese	Iron	Titanium	Boron	*Phosphorus*
#	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	*ppm*
187	11.5	0.015	0	0.1	0.5	0.6	0.2	min.	11
188	11.5	0.02	0	0.1	0.5	0.6	0.2	min.	11
189	11.5	0.03	0	0.1	0.5	0.6	0.2	min.	11
190	11.5	0.04	0	0.1	0.5	0.6	0.2	min.	11
191	11.5	0.05	0	0.1	0.5	0.6	0.2	min.	11
192	11.5	0	0.005	0.1	0.5	0.6	0.2	min.	11
193	11.5	0	0.01	0.1	0.5	0.6	0.2	min.	11
194	11.5	0	0.02	0.1	0.5	0.6	0.2	min.	11
195	11.5	0	0.025	0.1	0.5	0.6	0.2	min.	11
196	11.5	0	0.03	0.1	0.5	0.6	0.2	min.	11
197	11.5	0	0.04	0.1	0.5	0.6	0.2	min.	11
198	11.5	0	0.05	0.1	0.5	0.6	0.2	min.	11
Group Three (iii)									
199	11.5	0	0	min.	min.	min.	0.1	min.	6
200	11.5	0.005	0	min.	min.	min.	0.1	min.	6
201	11.5	0.04	0	min.	min.	min.	0.1	min.	6
202	11.5	0	0.005	min.	min.	min.	0.1	min.	6
203	11.5	0	0.05	min.	min.	min.	0.1	min.	6
204	11.5	0	0	min.	min.	min.	0.2	min.	11
Group Four									
205	10	0.015	0	min.	min.	min.	min.	0.05	-
206	10	0.015	0	min.	min.	min.	0.1	0.02	-
207	10	0.015	0	min.	min.	min.	0.2	0.05	-
208	10	0	0.025	min.	min.	min.	min.	0.05	-
209	10	0	0.025	min.	min.	min.	0.1	0.02	-
210	10	0	0.025	min.	min.	min.	0.2	0.05	-
211	11.5	0.015	0	min.	min.	min.	min.	0.05	-
212	11.5	0.015	0	min.	min.	min.	0.1	0.02	-
213	11.5	0.015	0	min.	min.	min.	0.2	0.05	-
214	11.5	0	0.025	min.	min.	min.	min.	0.05	-
215	11.5	0	0.025	min.	min.	min.	0.1	0.02	-
216	11.5	0	0.025	min.	min.	min.	0.2	0.05	-
217	13	0.015	0	min.	min.	min.	min.	0.05	-
218	13	0.015	0	min.	min.	min.	0.1	0.02	-
219	13	0.015	0	min.	min.	min.	0.2	0.05	-
220	13	0	0.025	min.	min.	min.	min.	0.05	-
221	13	0	0.025	min.	min.	min.	0.1	0.02	-
222	13	0	0.025	min.	min.	min.	0.2	0.05	-
Group Five									
223	12.7	0	0	min.	min.	min.	min.	0.05	-
224	12.7	0	0	min.	min.	min.	0.1	0.02	-
225	12.7	0	0	min.	min.	min.	0.2	0.05	-
226	12.7	0.007	0	min.	min.	min.	min.	0.05	-
227	12.7	0.007	0	min.	min.	min.	0.1	0.02	-
228	12.7	0.007	0	min.	min.	min.	0.2	0.05	-
229	12.7	0.015	0	min.	min.	min.	min.	0.05	-
230	12.7	0.015	0	min.	min.	min.	0.1	0.02	-
231	12.7	0.015	0	min.	min.	min.	0.2	0.05	-
232	12.7	0.04	0	min.	min.	min.	min.	0.05	-
233	12.7	0.04	0	min.	min.	min.	0.1	0.02	-
234	12.7	0.04	0	min.	min.	min.	0.2	0.05	-
235	12.7	0	0.01	min.	min.	min.	min.	0.05	-
236	12.7	0	0.01	min.	min.	min.	0.1	0.02	-
237	12.7	0	0.01	min.	min.	min.	0.2	0.05	-
238	12.7	0	0.025	min.	min.	min.	0.1	0.02	-
239	12.7	0	0.04	min.	min.	min.	0	0.05	-
240	12.7	0	0.04	min.	min.	min.	0.1	0.02	-
250	12.7	0	0.04	min.	min.	min.	0.2	0.05	-
Group Six									
251	12.7	0	0.025	0.1	min.	min.	0	0.05	-
252	12.7	0	0.025	0.1	min.	min.	0.1	0.02	-
253	12.7	0	0.025	0.1	min.	min.	0.2	0.05	-
254	12.7	0	0.025	min.	0.2	min.	0	0.05	-
255	12.7	0	0.025	min.	0.2	min.	0.1	0.02	-
256	12.7	0	0.025	min.	0.2	min.	0.2	0.05	-
257	12.7	0	0.025	min.	0.5	min.	0	0.05	-
258	12.7	0	0.025	min.	0.5	min.	0.1	0.02	-

Composition	Silicon	Sodium	Strontium	Magnesium	Manganese	Iron	Titanium	Boron	*Phosphorus*
#	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	*ppm*
259	12.7	0	0.025	min.	0.5	min.	0.2	0.05	-
260	12.7	0	0.025	min.	min.	0.6	0	0.05	-
261	12.7	0	0.025	min.	min.	0.6	0.1	0.02	-
262	12.7	0	0.025	min.	min.	0.6	0.2	0.05	-
263	12.7	0	0.025	min.	0.5	0.6	0	0.05	-
264	12.7	0	0.025	0.1	0.5	0.6	0.1	0.02	-
265	12.7	0	0.025	0.1	0.5	0.6	0.2	0.05	-
Group Seven									
266	12.7	0	0.025	min.	min.	min.	0	0.005	-
267	12.7	0	0.025	min.	min.	min.	0	0.02	-
268	12.7	0	0.025	min.	min.	min.	0	0.035	-
269	12.7	0	0.025	min.	min.	min.	0	0.05	-
270	12.7	0	0.025	0.1	0.5	0.6	0	0.005	-
271	12.7	0	0.025	0.1	0.5	0.6	0	0.02	-
272	12.7	0	0.025	0.1	0.5	0.6	0	0.035	-
273	12.7	0	0.025	0.1	0.5	0.6	0	0.05	-
274	12.7	0	0.025	min.	min.	min.	0.2	0.005	-
275	12.7	0	0.025	min.	min.	min.	0.2	0.02	-
276	12.7	0	0.025	min.	min.	min.	0.2	0.035	-
277	12.7	0	0.025	min.	min.	min.	0.2	0.05	-
278	12.7	0	0.025	0.1	0.5	0.6	0.2	0.005	-
279	12.7	0	0.025	0.1	0.5	0.6	0.2	0.02	-
280	12.7	0	0.025	0.1	0.5	0.6	0.2	0.035	-
281	12.7	0	0.025	0.1	0.5	0.6	0.2	0.05	-
Group Eight									
282	12.7	0	0.025	min.	min.	min.	0.02	0.02	-
283	12.7	0	0.025	min.	min.	min.	0.05	0.05	-
284	12.7	0	0.025	min.	min.	min.	0.1	0.05	-
285	12.7	0	0.025	min.	min.	min.	0.01	0.01	-
286	12.7	0	0.025	min.	min.	min.	0.01	0.05	-
287	12.7	0	0.025	min.	min.	min.	0.03	0.05	-
Group Nine									
288	13	0.015	0	0.1	0.5	0.6	0.1	0.02	-
289	13	0	0.025	0.1	0.5	0.6	0.1	0.02	-
290	13	0	0.03	0.1	0.5	0.6	0.1	0.02	-
291	12.7	0	0.025	min.	0.5	0.6	0.1	0.02	-
292	12.7	0	0.025	0.1	min.	0.6	0.1	0.02	-
293	12.7	0	0.025	0.1	0.5	min.	0.1	0.02	-

Appendix C

Enhanced Gas Bubble Extraction Due to Reduced Pressure

When a melt is subject to a change in surface pressure, the volume of entrained gas bubbles also changes. This adjusts the rate at which bubbles rise and are released into the atmosphere. The following calculations show the variation in bubble-rise velocity for surface pressures of 760, 100, 10 and 5 mm Hg respectively. The main assumption made is that evolved bubbles contain the same number of gas atoms irrespective of the surface pressure, e.g. PV = mRT = constant.

Change in bubble size due to pressure variations:

$$PV = \text{constant}$$

$$V \propto P^{-1}$$

and $$V = \frac{4}{3}\pi r^3$$

so $$V \propto r^3$$

$$\therefore P \propto r^{-3/3} \qquad \textbf{A.}$$

Force driving bubble to surface = bubble drag force (buoyancy):

$$V\rho g = \rho C_w A \frac{v^2}{2}$$

with $V = \frac{4}{3}\pi r^3$ and $A = \pi r^2$

therefore $$\frac{4}{3}\pi r^3 \rho g = \rho \frac{C_w \pi r^2}{2} v^2$$

or $$r = \frac{3}{8} C_w g^{-1} v^2$$

giving $$v \propto \sqrt{r} \qquad \textbf{B.}$$

(v = velocity, C_w = drag coefficient, etc..see Symbols Abbreviations and Units on page XI)

Combining A and B gives:

$$v \propto P^{-1/6} \qquad \textbf{C.}$$

The pressure exerted on the bubble will be the pressure head plus the surface pressure.

$$P = P_{surface} + P_{head}$$

$$= P_{surface} + \rho gh$$

or if P is entered as mm Hg

$$P = P_{surface} + 200h \qquad \textbf{D.}$$

(h in m Al, P in mm Hg, e.g. 1m Al = 200 mm Hg)

Combining C and D:

$$v \propto (\text{Psurface} + 200\text{h})^{-1/6} \qquad \textbf{E.}$$

This may be integrated to give the average velocity over a given head:

$$v_{ave} \propto \int (Psurface + 200\,h)^{-1/6}\, dh$$

$$v_{ave} \propto \left[\frac{1}{166.6}(Psurface + 200\,h)^{5/6}\right]_{h_1}^{h_2}$$

$$v_{ave} \propto \left[(Psurface + 200\,h)^{5/6}\right]_{h_1}^{h_2} \qquad \textbf{F.}$$

Using expressions E and F the following results can be calculated. It should be noted that the actual velocities can not be calculated, only relative changes.

	Velocity(in Brackets) and Velocity Increase(%) Values		
	Using Eqn E.		**Using Eqn F.**
	h = 0 i.e. at melt surface	h = 1 i.e. 1m below melt surface	Average velocity increase over 1m head.
P*surface* =Patm =760mmHg	(reference velocity =0.3310)	(reference velocity =0.3184)	(reference velocity =54.05)
P*surface* =100mmHg	**40.20%** (0.4642)	**21%** (0.3865)	**28.70%** (69.5)
P*surface* =10mmHg	**105%** (0.6813)	**29%** (0.4102)	**46.80%** (79.3)
P*surface* =5mmHg	**131%** (0.7647)	**29%** (0.4118)	**49.10%** (80.6)

Appendix D

Melt Contamination Due to Various Degassing Lances.

-Melt initially 400g of commercially pure aluminium (99.85%Al).

Melt Exposure	Silicon	Std. Dev.	Iron	Std. Dev.	Manganese	Std. Dev.
Period (min.)	%		%		%	
Mild Steel Lance						
0	0.045	0.0017	0.1382	0.0074	0.0012	0
5	0.0394	0.0029	2.1844	0.2019	0.015	0.0007
10	0.0466	0.0056	3.6213	0.2029	0.0243	0.0008
15	0.0452	0.002	5.52	0.6321	0.0368	0.001
20	0.0513	0.0005	5.4342	0.4334	0.042	0.0015
Stainless Steel Lance						
0	0.045	0.0017	0.1382	0.0074	0.0012	0
5	0.066	0.0025	2.4485	0.0436	0.0506	0.0011
10	0.0797	0.0105	2.9803	1.8776	0.1027	0.03
15	0.0786	0.001	4.5165	0.4248	0.0895	0.0063
20	0.084	0.003	4.8128	0.4094	0.0955	0.0064
Refractory Coated Mild Steel Lance						
0	0.045	0.0017	0.1382	0.0074	0.0012	0
5	0.0443	0.0006	0.4793	0.0061	0.0029	0
10	0.0404	0.0023	1.244	0.0268	0.0084	0.0001
15	0.0506	0.0021	2.0403	0.0251	0.0134	0
20	0.0543	0.0024	3.4108	0.4059	0.0225	0.0015
Refractory Coated Stainless Steel Lance						
0	0.045	0.0017	0.1382	0.0074	0.0012	0
5	0.0459	0.0037	0.4842	0.0556	0.0077	0.0002
10	0.0509	0.0026	0.9353	0.0156	0.0163	0.0002
15	0.0632	0.0035	1.6391	0.0152	0.0326	0.0002
20	0.0709	0.0035	1.8533	0.0659	0.0373	0.0013
Graphite Lance						
0	0.045	0.0017	0.1382	0.0074	0.0012	0
5	0.0448	0.0031	0.1429	0.0143	0.0011	0.0001
10	0.0446	0.0008	0.1321	0.0052	0.0012	0
15	0.0484	0.0015	0.1329	0.0052	0.0012	0.0001
20	0.0476	0.0017	0.128	0.0071	0.0013	0.0001
Ceramic Lance						
0	0.045	0.0017	0.1382	0.0074	0.0012	0
5	0.0449	0.0053	0.1337	0.0225	0.0013	0
10	0.048	0.0009	0.1372	0.0023	0.0011	0
15	0.0544	0.001	0.1488	0.0064	0.0012	0
20	0.0547	0.0016	0.1536	0.0067	0.0013	0

Appendix E

Melt Composition Variation During Degassing.

-Each successive sample in the following sample sets is separated by 1.5 minutes of degassing time or 1/3 the recommended solid degasser addition.

-No lithium, berilium, bismuth or zerconium was detected in any of the following samples.

Sample	Silicon	Iron	Copper	Magnesium	Zinc	Nickel	Manganese	Lead	Chromium	Titanium	Tin	Calcium	Sodium	Vanadium	Galium	Boron	Strontium
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Argon Degassed Samples																	
A1																	
A2	11.8939	0.5852	0.0027	0.0909	0.1088	0.002	0.4607	0.0014	0.0012	0.0222	0.0012	0	0.0001	0.0065	0.0089	0.0011	0
A3	11.9342	0.5917	0.0032	0.0903	0.1084	0.002	0.4739	0.0015	0.0012	0.0237	0.0012	0.0005	0.0005	0.0066	0.009	0.0015	0
A4	11.9249	0.5956	0.0033	0.0893	0.1081	0.002	0.4815	0.0016	0.0013	0.0226	0.0012	0	0	0.0066	0.0089	0.0012	0
A5	11.9666	0.5951	0.0036	0.0894	0.1087	0.002	0.4829	0.0017	0.0013	0.0213	0.0012	0.0001	0.0001	0.0066	0.009	0.0008	0
A6	11.7803	0.5975	0.0038	0.0896	0.1072	0.002	0.4928	0.0019	0.0014	0.0211	0.0012	0	0	0.0065	0.0089	0.0007	0
A7	11.8026	0.5951	0.004	0.0861	0.1075	0.002	0.4922	0.002	0.0014	0.0209	0.0012	0	0	0.0066	0.0089	0.0007	0
A8	11.836	0.5983	0.0042	0.0861	0.1079	0.0021	0.4952	0.002	0.0015	0.0204	0.0012	0	0	0.0066	0.009	0.0005	0
A9	11.8124	0.599	0.0044	0.0846	0.1072	0.002	0.4947	0.002	0.0014	0.0199	0.0012	0	0.0001	0.0065	0.0089	0.0003	0
A10	11.9737	0.6027	0.0044	0.0855	0.1082	0.002	0.4961	0.002	0.0015	0.02	0.0012	0	0.0001	0.0067	0.009	0.0004	0
Sodium Modified Argon Degassed Samples																	
ANA1	12.2969	0.5601	0.0037	0.0946	0.1166	0.0031	0.4771	0.0014	0.0042	0.0243	0.001	0.0001	0.0318	0.0072	0.0099	0.0023	0
ANA2	12.1584	0.596	0.0035	0.0783	0.1118	0.0031	0.4995	0.0014	0.0041	0.0226	0.0011	0	0.0129	0.0068	0.0093	0.0015	0
ANA3	12.1957	0.6116	0.0035	0.0698	0.11	0.0032	0.5037	0.0014	0.0043	0.0218	0.0012	0.0003	0.0058	0.0069	0.0091	0.0011	0
ANA4	12.1076	0.6121	0.0035	0.0674	0.1096	0.0032	0.5052	0.0015	0.0043	0.0208	0.0012	0	0.0033	0.0069	0.009	0.0008	0
ANA5	12.0998	0.6191	0.0036	0.0674	0.1107	0.0033	0.5073	0.0015	0.0041	0.0207	0.0012	0	0.0018	0.0066	0.0092	0.0008	0
ANA6	11.9906	0.6132	0.0035	0.0626	0.1094	0.0034	0.5041	0.0016	0.0045	0.0195	0.0012	0	0.0005	0.0067	0.009	0.0003	0
ANA7	11.9388	0.6077	0.0035	0.0612	0.1091	0.0034	0.4997	0.0017	0.0047	0.0199	0.0012	0	0.0002	0.0067	0.009	0.0004	0
ANA8	11.985	0.6134	0.0035	0.0601	0.1091	0.0034	0.5024	0.0017	0.0047	0.0192	0.0012	0	0.0002	0.0065	0.009	0.0002	0
ANA9	11.9474	0.6196	0.0035	0.0596	0.109	0.0035	0.5036	0.0017	0.0048	0.0189	0.0012	0	0.0002	0.0067	0.009	0.0001	0
ANA10	11.8457	0.615	0.0034	0.0579	0.1081	0.0034	0.4987	0.0017	0.0046	0.0186	0.0012	0	0.0001	0.0064	0.0089	0	0
Strontium Modified Argon Degassed Samples																	
ASR1	12.0896	0.5568	0.0025	0.1	0.1108	0.0016	0.4546	0.0011	0.0005	0.0233	0.0011	0.0001	0.0001	0.0069	0.0091	0.0016	0.0319
ASR2	12.0363	0.5826	0.0031	0.1002	0.1113	0.0016	0.4759	0.0012	0.0005	0.021	0.0012	0	0	0.007	0.0091	0.0008	0.0308
ASR3	12.0559	0.5877	0.0036	0.0991	0.1107	0.0016	0.4785	0.0013	0.0005	0.0208	0.0012	0.0004	0.0007	0.0068	0.0091	0.0008	0.0298
ASR4	12.067	0.5349	0.0044	0.0992	0.1104	0.0016	0.4796	0.0013	0.0006	0.0211	0.0012	0	0	0.0069	0.0091	0.0009	0.0297
ASR5	12.0551	0.5889	0.0047	0.0988	0.1103	0.0016	0.4806	0.0013	0.0005	0.0201	0.0012	0	0.0001	0.0066	0.0091	0.0006	0.0291
ASR6	12.0726	0.5865	0.0051	0.0977	0.1098	0.0016	0.484	0.0015	0.0006	0.0206	0.0012	0.0002	0.0004	0.0066	0.009	0.0008	0.029
ASR7	12.101	0.5898	0.0053	0.0965	0.1097	0.0016	0.4806	0.0015	0.0006	0.0197	0.0012	0	0	0.0067	0.009	0.0004	0.0276
ASR8	12.0351	0.5907	0.0054	0.0956	0.1094	0.0017	0.4793	0.0016	0.0008	0.0191	0.0012	0.0002	0.0001	0.0066	0.009	0.0003	0.0263
ASR9	12.1008	0.5961	0.0056	0.0966	0.11	0.0017	0.4825	0.0016	0.0007	0.0188	0.0012	0.0001	0.0002	0.0068	0.0091	0.0001	0.0256
ASR10	12.1734	0.5987	0.0058	0.0967	0.1101	0.0017	0.4842	0.0016	0.0006	0.0192	0.0012	0.0001	0.0003	0.0065	0.0091	0.0001	0.0248

Sample	Silicon	Iron	Copper	Magnesium	Zinc	Nickel	Manganese	Lead	Chromium	Titanium	Tin	Calcium	Sodium	Vanadium	Galium	Boron	Strontium
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Nitrogen Degassed Samples																	
N1	12.1096	0.2197	0	0.0999	0.1132	0.0021	0.1317	0.0002	0.0018	0.0253	0.0009	0.0001	0.0002	0.0065	0.0088	0.0017	0
N2	11.994	0.6963	0.0002	0.0951	0.1124	0.0025	0.4817	0.0009	0.0024	0.0221	0.0012	0	0	0.0066	0.009	0.001	0
N3	12.0657	0.7069	0.0002	0.0964	0.1127	0.0027	0.5002	0.001	0.0026	0.0223	0.0012	0	0	0.0065	0.0091	0.0011	0
N4	12.0269	0.7045	0.002	0.0932	0.1117	0.0027	0.5028	0.0009	0.0027	0.0212	0.0012	0	0	0.0065	0.0089	0.0007	0
N5	12.1101	0.7132	0.0002	0.0929	0.1119	0.0027	0.5088	0.001	0.0028	0.0213	0.0012	0	0.0001	0.0066	0.0089	0.0007	0.0001
N6	12.0839	0.7114	0.0002	0.09	0.1123	0.0029	0.5096	0.0011	0.0032	0.02	0.0013	0	0	0.0065	0.0089	0.0003	0
N7	12.1433	0.7117	0.0003	0.089	0.1128	0.003	0.5088	0.0012	0.0035	0.0198	0.0013	0	0.0001	0.0067	0.009	0.0002	0
N8	11.9085	0.7025	0.0003	0.088	0.1111	0.003	0.5063	0.0012	0.0035	0.0199	0.0013	0	0.0001	0.0063	0.0089	0.0004	0
N9	11.9925	0.712	0.0004	0.0861	0.111	0.0031	0.5113	0.0011	0.0036	0.0195	0.0013	0	0	0.0066	0.0089	0.0002	0
N10	12.0475	0.7128	0.0003	0.0849	0.1102	0.0031	0.5125	0.0011	0.0036	0.0193	0.0013	0	0	0.0063	0.0088	0.0001	0
Sodium Modified Nitrogen Degassed Samples																	
NNA1	12.3837	0.5827	0.0002	0.094	0.1215	0.0037	0.4441	0.0009	0.0054	0.0225	0.001	0	0.0301	0.0068	0.0097	0.0015	0
NNA2	12.2527	0.6146	0.0002	0.081	0.1178	0.0039	0.468	0.0009	0.0056	0.0211	0.0011	0	0.0128	0.0066	0.0093	0.0009	0
NNA3	12.1718	0.6298	0.0002	0.0747	0.1147	0.0039	0.4749	0.001	0.0057	0.0216	0.0011	0	0.0066	0.0064	0.009	0.001	0
NNA4	12.3173	0.6399	0.0003	0.0742	0.1149	0.004	0.4829	0.001	0.0057	0.0213	0.0012	0	0.0036	0.0065	0.0089	0.0008	0
NNA5	12.2785	0.6454	0.0002	0.0719	0.1155	0.004	0.4828	0.001	0.0057	0.0208	0.0012	0	0.0018	0.0064	0.009	0.0006	0
NNA6	12.103	0.635	0.0003	0.0687	0.1148	0.0043	0.4776	0.001	0.0061	0.0197	0.0012	0	0.0006	0.0064	0.009	0.0002	0
NNA7	11.9993	0.6347	0.0002	0.647	0.113	0.0043	0.4759	0.001	0.0063	0.0195	0.0012	0	0.0002	0.0063	0.0088	0.0002	0
NNA8	12.0686	0.6286	0.0003	0.0645	0.1141	0.0045	0.4724	0.001	0.0066	0.0195	0.0012	0	0.0001	0.0064	0.0089	0.0001	0
NNA9	11.8775	0.6346	0.0003	0.0622	0.1124	0.0044	0.4754	0.001	0.0067	0.0193	0.0013	0	0.0001	0.0064	0.0087	0.0001	0
NNA10	11.9272	0.6335	0.0003	0.0617	0.1127	0.0045	0.4748	0.001	0.0067	0.0191	0.0012	0	0.0001	0.0063	0.0088	0	0
Strontium Modified Nitrogen Degassed Samples																	
NSR1	12.1664	0.5286	0.0002	0.1001	0.1096	0.0027	0.4191	0.0007	0.003	0.0236	0.0012	0.0004	0.0006	0.0067	0.0092	0.0015	0.0333
NSR2	12.1994	0.6038	0.0002	0.099	0.1094	0.0029	0.4779	0.001	0.0034	0.0232	0.0012	0.0001	0.0001	0.0069	0.0092	0.0015	0.0333
NSR3	12.021	0.6009	0.0002	0.0957	0.1082	0.003	0.4761	0.0011	0.0035	0.0206	0.0012	0	0.0001	0.0068	0.0091	0.0007	0.0308
NSR4	12.1135	0.6038	0.0003	0.0959	0.1088	0.0031	0.4797	0.0011	0.0037	0.0199	0.0012	0.0001	0.0001	0.0068	0.0091	0.0004	0.0305
NSR5	12.1492	0.6066	0.0002	0.0955	0.1088	0.0031	0.4812	0.0011	0.038	0.0198	0.0012	0	0.0001	0.0068	0.0091	0.0004	0.0299
NSR6	12.0913	0.6081	0.0002	0.0932	0.1085	0.0032	0.4843	0.0012	0.004	0.019	0.0012	0.0001	0.0002	0.0065	0.0091	0.0002	0.0275
NSR7	12.0913	0.6091	0.0002	0.0927	0.1081	0.0034	0.4842	0.0012	0.0044	0.0195	0.0012	0	0.0001	0.0066	0.0091	0.0003	0.0275
NSR8	12.0692	0.6089	0.0002	0.091	0.1079	0.0035	0.4837	0.0012	0.0047	0.0187	0.0012	0	0.0001	0.0067	0.0091	0.0001	0.0261
NSR9	12.1092	0.6101	0.0003	0.0908	0.108	0.0036	0.484	0.0012	0.0048	0.0187	0.0012	0	0.0001	0.0065	0.0091	0.0001	0.0253
NSR10	12.1331	0.6119	0.0003	0.0907	0.1081	0.0036	0.4847	0.0012	0.005	0.0186	0.0012	0	0.0001	0.0067	0.0091	0	0.0247
Samples Degassed with Foseco "Degasser 190"																	
1901	12.1277	0.1444	0	0.0292	0.1069	0.0014	0.0169	0.0001	0.0003	0.0264	0.001	0	0.0001	0.0065	0.0085	0.003	0
1902	11.9476	0.6907	0.0003	0.0281	0.1077	0.0018	0.4955	0.001	0.0008	0.0262	0.0014	0	0	0.0069	0.009	0.0024	0
1903	11.9432	0.709	0.0001	0.0228	0.1065	0.0018	0.4983	0.001	0.0008	0.026	0.0014	0	0	0.0066	0.0088	0.0013	0
1904	12.034	0.7189	0.0002	0.0186	0.1069	0.0019	0.5009	0.001	0.0011	0.0254	0.0014	0	0	0.0069	0.0089	0.0023	0
1905	12.0479	0.7152	0.0003	0.0159	0.1071	0.0019	0.5	0.0011	0.0009	0.0244	0.0013	0	0.0001	0.0069	0.0089	0.002	0
1906	11.9111	0.7171	0.0002	0.0122	0.1073	0.0019	0.5007	0.0013	0.001	0.0252	0.0014	0	0.0001	0.0067	0.009	0.0024	0
1907	11.9512	0.7192	0.0003	0.0098	0.1073	0.0019	0.5019	0.0011	0.0011	0.0229	0.0014	0	0.0001	0.0068	0.0089	0.0017	0
1908	12.0694	0.7259	0.0003	0.0087	0.1066	0.002	0.5042	0.0012	0.0011	0.0216	0.0014	0	0.0003	0.0068	0.0088	0.0013	0

Sample	Silicon	Iron	Copper	Magnesium	Zinc	Nickel	Manganese	Lead	Chromium	Titanium	Tin	Calcium	Sodium	Vanadium	Galium	Boron	Strontium
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
1909	12.0189	0.7231	0.0004	0.0058	0.1068	0.0019	0.5039	0.0012	0.0011	0.0214	0.0014	0	0	0.0066	0.0088	0.0013	0
19010	12.0414	0.7223	0.0003	0.0054	0.1068	0.0019	0.5024	0.0014	0.0011	0.0219	0.0013	0.0001	0.0002	0.0064	0.0088	0.0016	0
Sodium Modified Samples Degassed with Foseco "Degasser 190"																	
190NA1	12.3347	0.6045	0.0001	0.0287	0.1118	0.0028	0.1721	0.0008	0.0044	0.0237	0.001	0	0.0196	0.0069	0.0092	0.0017	0
190NA2	12.2639	0.6222	0.0003	0.0253	0.1103	0.0028	0.1752	0.0009	0.0056	0.0237	0.001	0	0.0111	0.0068	0.0091	0.0016	0
190NA3	12.1957	0.6284	0.0001	0.0217	0.1089	0.0028	0.1757	0.0009	0.0046	0.0222	0.0011	0	0.007	0.0065	0.0088	0.0012	0
190NA4	12.3369	0.6372	0.0001	0.0188	0.1084	0.0029	0.1764	0.0014	0.0049	0.0228	0.0012	0	0.0049	0.0068	0.0088	0.0012	0
190NA5	12.2949	0.6363	0.0001	0.0159	0.1079	0.0029	0.176	0.0011	0.0049	0.0216	0.0012	0.0001	0.003	0.0066	0.0087	0.001	0
190NA6	12.1986	0.6305	0.0001	0.0128	0.1078	0.0029	0.1747	0.001	0.0048	0.0229	0.0012	0	0.0016	0.0067	0.0087	0.0015	0
190NA7	12.1126	0.6347	0.0003	0.0102	0.1075	0.0029	0.1755	0.001	0.0048	0.0214	0.0012	0	0.0009	0.0065	0.0087	0.0011	0
190NA8	12.0822	0.6352	0.0001	0.0084	0.1072	0.0029	0.175	0.0036	0.0052	0.0225	0.0013	0	0.0006	0.0067	0.0087	0.0014	0
190NA9	11.9452	0.6339	0.0002	0.0064	0.1066	0.0029	0.1748	0.001	0.0047	0.0208	0.0012	0.0001	0.0006	0.0063	0.0086	0.001	0
190NA10	12.0098	0.6397	0.0002	0.0048	0.1077	0.003	0.1757	0.0011	0.0048	0.0201	0.0012	0.0003	0.0005	0.0063	0.0088	0.0008	0
Samples Degassed with Foseco "Degasser 610"																	
6101	11.9109	0.2009	0.0001	0.1011	0.1097	0.0019	0.1822	0.0003	0.0012	0.0251	0.0011	0	0.0001	0.0069	0.0091	0.0018	0
6102	11.8987	0.5797	0.0003	0.0951	0.1084	0.0021	0.464	0.0009	0.0016	0.0238	0.0013	0.0001	0.0002	0.0069	0.009	0.0015	0
6103	11.9415	0.5834	0.002	0.0921	0.1077	0.0021	0.4788	0.0009	0.0016	0.0231	0.0013	0.0003	0.0004	0.0072	0.0089	0.0013	0
6104	11.8998	0.5893	0.0004	0.0916	0.108	0.002	0.4851	0.0009	0.0014	0.0227	0.0013	0	0.0001	0.0067	0.0089	0.0012	0
6105	11.8674	0.5972	0.0001	0.0938	0.1086	0.0021	0.4888	0.001	0.0015	0.023	0.0013	0	0.0001	0.007	0.0091	0.0014	0
6106	11.9886	0.5969	0.0003	0.0891	0.1079	0.0021	0.4866	0.001	0.0016	0.0222	0.0013	0.0003	0.0004	0.0069	0.009	0.001	0
6107	11.9082	0.6053	0.0002	0.0878	0.1082	0.0021	0.4906	0.001	0.0014	0.0212	0.0013	0	0.0001	0.0066	0.009	0.0007	0
6108	11.914	0.6083	0.0002	0.0876	0.1086	0.0022	0.4894	0.001	0.0015	0.0212	0.0013	0	0.0001	0.0066	0.0091	0.0007	0
6109	11.8762	0.604	0.0002	0.0851	0.1076	0.0021	0.4864	0.001	0.0015	0.0211	0.0013	0	0	0.0068	0.0089	0.0007	0
61010	12.0074	0.616	0.0002	0.0846	0.1081	0.0022	0.4897	0.0011	0.0018	0.0206	0.0013	0	0.0001	0.0067	0.0089	0.0005	0
Strontium Modified Samples Degassed with Foseco "Degasser 610"																	
610SR1	12.1621	0.5558	0.0005	0.0977	0.1129	0.002	0.3801	0.0011	0.0014	0.0243	0.0012	0	0.0001	0.0069	0.0091	0.0018	0.0332
610SR2	12.0721	0.6441	0.0005	0.0959	0.1123	0.0021	0.4775	0.001	0.0014	0.0214	0.0013	0	0.0001	0.0066	0.009	0.0009	0.0316
610SR3	12.0465	0.6473	0.0005	0.0947	0.112	0.0021	0.4797	0.0011	0.0015	0.02	0.0013	0	0.0001	0.0066	0.009	0.0005	0.0303
610SR4	12.2716	0.6517	0.0005	0.0963	0.1133	0.0021	0.4831	0.0011	0.0017	0.0203	0.0013	0	0.0001	0.0069	0.0091	0.0005	0.0303
610SR5	12.1552	0.6544	0.0005	0.0949	0.1124	0.0021	0.4844	0.0011	0.0017	0.0199	0.0013	0.0001	0.0001	0.0068	0.009	0.0004	0.0301
610SR6	12.2545	0.667	0.0006	0.1003	0.1149	0.0024	0.489	0.0013	0.0021	0.0205	0.0013	0.0001	0.0001	0.0069	0.0093	0.0002	0.0268
610SR7	12.2541	0.6653	0.0005	0.0965	0.1144	0.0023	0.4851	0.0013	0.0021	0.02	0.0013	0.0001	0.0002	0.0067	0.0091	0.0002	0.026
610SR8	12.2153	0.666	0.0005	0.0934	0.1126	0.0023	0.4857	0.0012	0.002	0.0193	0.0013	0	0.0001	0.0066	0.009	0.0002	0.0249
610SR9	12.0813	0.6637	0.0005	0.0926	0.1126	0.0023	0.484	0.0012	0.0021	0.0189	0.0013	0	0.0001	0.0067	0.0089	0.0001	0.0239
610SR10	12.2708	0.6686	0.0005	0.0933	0.1131	0.0023	0.4849	0.0013	0.0022	0.0196	0.0013	0.0007	0.002	0.0068	0.009	0.0003	0.0239

Appendix F
Specifications of Melt Addition Products

Base Alloys

CA401F

Function: CA401F is a high-purity virgin aluminium-silicon eutectic alloy. This alloy was chosen as the base constituent to which other impurities and alloys were added.

Supplier: New Zealand Aluminium Smelters Ltd, New Zealand

Manufacturer: New Zealand Aluminium Smelters Ltd, New Zealand

Composition: The following composition is from the NZAS Certificate of Analysis.

	Up to Melt 134	Beyond Melt 134
Aluminium	Remainder %	Remainder
Silicon	12.6%	12.7%
Iron	0.19%	0.18%
Copper	0.00%	0.00%
Magnesium	0.00%	0.00%
Zinc	0.00%	0.00%
Nickel	0.00%	0.00%
Manganese	0.00%	0.00%
Titanium	0.01%	0.01%
Calcium	0.000%	0.000%
Sodium	0.000%	0.000%
Gallium	0.01%	0.01%
Form:	19 kg ingots	15 kg ingots

ZP190B

Function: ZP190B is a high-purity virgin aluminium alloy produced without refining after the primary smelter. This alloy was chosen as an additive to reduce silicon levels below the 12.6%Si of the 401(above) without adding excessive additional impurity.

Supplier: New Zealand Aluminium Smelters Ltd, New Zealand

Manufacturer: New Zealand Aluminium Smelters Ltd, New Zealand

Composition: The following composition is from the NZAS Certificate of Analysis.

Aluminium	99.91%
Silicon	0.028%

	Iron	0.049%
	Copper	0.000%
	Magnesium	0.000%
	Zinc	0.002%
	Nickel	0.002%
	Manganese	0.001%
	Lead	0.001%
	Chromium	0.000%
	Titanium	0.000%
	Tin	0.001%
	Other	0.014%
Form:	22.5 kg ingots	

Additional Alloys

Al-25Si

Function: Al-25Si is a master alloy created by the addition of silicon to primary aluminium. As such, it contains relatively low levels of impurities other than silicon. This alloy was used to boost the base 401 silicon level to 13% and to replace silicon lost during degassing. Addition took place prior to degassing.

Supplier: W M Scollay & Co Ltd, New Zealand

Manufacturer: Kawecki-Billiton Metaalindustrie B.V., The Netherlands

Composition: The following analysis is that given by KBM Information Sheet SI.03.E[156]. Individual analysis sheets were provided for each batch supplied, giving actual Si, Fe and Cu levels. These values are shown in brackets.

Aluminium	Remainder	
Silicon	23-27%	(24.9%, 26.6%, 23.7%)
Iron	0.50 max	(0.24%, 0.31%, 0.29%)
Calcium	0.10 max	
Others	0.05 max	

Form: 7 kg waffle ingot and 1 kg sections thereof.

Navac 25 (Na)

Function: Foseco "Navac 25" capsules consist of 25g of pure sodium vacuum packed into airtight aluminium canisters. These capsules are designed to be added whole to the melt, so modifying and refining the form of eutectic silicon. Due to the small size of the melts used in this investigation the capsules were opened and the sodium extracted to the relevant weight then tightly repacked in aluminium foil. this was carried out immediately prior to sodium use.

Supplier: Foseco New Zealand Ltd

Manufacturer: Foseco (F.S.) Limited, England

Composition: No documentation available, believed to be:

Sodium (metallic) 99.9% plus flux

Form: Aluminium capsules containing 25g pure sodium plus flux.

Al-10%Sr

Function: Aluminium strontium rod was added to modify the eutectic silicon in the same manner as sodium. The master alloy was added in rod form due to its superior reaction rate and gassing effects compared to the alternate waffle blocks.

Supplier: New Zealand Aluminium Smelters Ltd, New Zealand

Manufacturer: Kawecki-Billiton Metaalindustrie B.V., The Netherlands

Composition: the following data comes from NZAS supply data and KBM Information Sheet SR.2.E[29].

Aluminium	Remainder
Strontium	9-11%
Iron	0.1% max
Silicon	0.03% max
Other	0.03% max each

Form: 9.5mm diameter rod (full coil minimum length 937m).

Magnesium

Function: Pure metallic magnesium was added to the relevant melts immediately following degassing. Magnesium is generally added to strengthen heat treatable alloys.

Supplier: New Zealand Aluminium Smelters Ltd, New Zealand

Manufacturer: Norsk Hydro A.S., Norway

Composition: The following comes from the relevant Hydro supply invoice and NZAS raw material specifications. This product complies with ASTM982-61 9980A.

Magnesium	99.8%
Aluminium	0.01%
Manganese	0.009%
Silicon	0.007%
Iron	0.03%
Copper	0.02%
Nickel	0.001%
Lead	0.01% max
Tin	0.01% max

Form: 8 kg ingot

Al-75%Mn and Al-50%Fe

Function: Powder briquettes were added to certain melts prior to degassing so as to simulate the use of secondary charge material. Manganese and/or iron levels were boosted to 0.2%, 0.5% or 0.6% as described in Chapter 3.

Supplier: New Zealand Aluminium Smelters Ltd, New Zealand

Manufacturer: London & Scandinavian Metallurgical Co Ltd, England

Composition: The only information available on these products came from NZAS Raw Material Specifications.

	Al-75%Mn	Manganese 74-76% (99.9% Mn powder)
and	Al-50%Fe	Iron 49-51% (99.9% Fe powder)
each with a balance consisting		Aluminium powder, non-hygroscopic sodium-free binders and various fluxes.

Form: Compacted powder briquettes

Al-75%Ti

Function: Titanium was added primarily as a grain refiner. Like sodium and strontium it is subject to fade with time so several additions were required in some melts. Addition of aluminium-titanium compacted powders took place prior to degassing.

Supplier: New Zealand Aluminium Smelters Ltd, New Zealand

Manufacturer: Hoesch, Giessereichemie und Metallurgie GMBH, Germany

Composition: The following are the composition requirements of the NZAS Raw Material Specifications.

Titanium	74-76%
Iron	0.3% max
Silicon	0.2% max
Vanadium	0.2% max
Balance	Aluminium powder, non-hygroscopic Na-free flux and binders
Others	0.02% max
Other Total	0.10% max

Form: Aluminium foil wrapped 667g compressed powder tablets.

Al-5%Ti-1%B ("Tibor")

Function: "Tibor" was added as a grain refiner. Addition of this master alloy rod took place prior to degassing at the same time as iron, manganese, titanium and boron additions.

Supplier: CWF Hamilton Ltd, New Zealand and WM Scollay & Co Ltd, New Zealand

Manufacturer: Kawecki-Billiton Metaalindustrie BV, The Netherlands

Composition: Little information was obtained regarding the exact composition of this master alloy, however the nominal composition is:

Aluminium	94%	(based on 99.7% aluminium)
Titanium	5%	
Boron	1%	

Form: 9.5 mm diameter rod in 50 cm lengths.

Al-3%B

Function: Boron is often added to combine with Ti, Zr, Cr and V forming dense precipitates which sink to the bottom of the melt for latter extraction. Alloys of this type contain predominantly AlB_{12} compounds. The AlB3 master alloy used was requested to be of the AlB_2 type, which is known to be a powerful grain refiner in certain alloys. Unfortunately, subsequent to production of all final test pieces the supplied alloy was found to be of the AlB_{12} type. Boron additions took place prior to degassing.

Supplier: Austral Bronze Crane Copper Ltd, Australia

Manufacturer: Kawecki-Billiton Metaalindustrie BV, The Netherlands

Composition: The following composition data comes from the DBM analysis report provided with the ingot.

Aluminium	Remainder
Boron	2.8%
Iron	0.12%
Silicon	0.06%
Titanium	0.02%

Form: 7 kg waffle ingot and portions thereof.

CuP

Function: To boost phosphorus levels in the relevant samples CuP shot was added to some melts immediately following degassing. This product was only used on a limited number of samples.

Supplier: Foseco New Zealand Ltd, New Zealand

Manufacturer: Foseco (FS) Limited, England

Composition: The analysis below was supplied by NZAS. It is for the shot only (the only product added).

Copper	85.7%
Phosphorus	13.9%
Remainder	Unspecified

Form: Sealed copper tubes containing CuP shot.

Appendix G
Micro and Macro Etchants

The following etchants have been evaluated during the course of the current research. These have emanated from several texts, the more significant being:

- 9th Ed. Metals Handbook.
- Metallographic Determination of Intermetallic Compounds in Aluminium Alloys (Ref 161).
- Metallographic Atlas of Cast Aluminium Alloys (Ref 144).

Micro Etchants

(1) Kellers Reagent

2 ml	HF (48%)	}	
3 ml	HCl conc.	}	Swab for 15 seconds
5 ml	HNO_3 conc.	}	at room temp.
190 ml	H_2O	}	

This reagent highlighted the $FeSiAl_5$, $(Fe\ Mn)_3Si_2Al_{15}$ and Mg_2Si phases in black, light brown and black respectively.

(2)

1 ml	HF (48%)	}	Swab for 15 seconds
200 ml	H_2O	}	at room temp.

This very common etch revealed precipitates in a very similar manner to Kellers Reagent. It had an advantage over Kellers Reagent in that it was easier to prepare.

(3) Wassermans Reagent

0.5 ml	HF (60%)	}	
1 ml	HNO_3	}	Swab breifly
50 ml	$K_2Cr_2O_7$ (10%)	}	at room temp.
100 ml	H_2O	}	

This etch only worked well when freshly mixed. The manganese, magnesium and iron compounds were highlighted with dark shades, particularly in the eutectic regions.

(4)

10 ml	H_2SO_4 conc.	} Immerse sample in
70 ml	H_2O	} warm etch ($\approx 40^{\circ}C$)

Samples immersed in this solution displayed very clear dark $FeSiAl_5$ needles. Stronger forms of this reagent were tried and even darker (black) iron compounds were produced. With only concentrated H_2SO_4 large numbers of black iron needles were revealed in samples containing high levels of iron (0.6%). As expected samples containing high levels of both iron and manganese displayed significantly less iron needles than samples high in iron alone.

(5) Modified Murakami Reagent

5 g	$K_3Fe(CN)_6$	} 2 mins immersion
10 g	NaOH	} & 10 secs immersion
60 ml	H_2O	} at room temp.

It is suggested that this etchant, put forward by Heinz and Klemm[172], can be used to reveal eutectic aluminium subgrain boundaries. Samples etched with this agent viewed at magnifications of 500-800x, contained dark bands within the eutectic aluminium, however, these bands were not sharply defined. Repeated attempts to produce distinct subgrain structures were not successful, suggesting that the effectiveness of this etchant may be affected by the presence of impurity elements. When exposed for shorter periods than originally suggested (i.e. 10 secs) this agent proved very effective at staining iron needles black.

Macro Etchants

(1) Poultons Etch

10 ml	HF (48%)	}
120 ml	HCl conc.	} Brief immersion
60 ml	HNO_3 conc.	} at room temp.
10 ml	H_2O	}

This extremely potent etchant rapidly pitted the alloy surface revealing distinct grain boundaries. The clarity of individual grain boundaries was dependent on the angle of incident light. Not all grains could be clearly defined at one time using conventional light sources. Cross-polarised light did not assist grain definition; light of varying colour projected from varying angles did. While being effective this solution seemed to offer no advantages over iron-chloride solution (discussed later).

(2) Tuckers Reagent

45	HCl conc.	}
15	HNO_3 conc.	} Immerse 10-15 secs
15	HF (48%)	}
25	H_2O	}

Tuckers Reagent worked in the same manner as Poultons Etch except, the reaction was slower and more reaction precipitates formed on the etched surface reducing the clarity of the revealed structure.

(3)

10 ml	HF (48%)	} Immerse then rinse
90 ml	H_2O	} under hot water

This solution was exceedingly slow to react, it seemed to react with little more vigour than 0.5% HF micro etch! Grain boundaries were not clearly revealed.

(4) & (5)

60 ml	HCl conc.		90 ml	HCl conc.
60 ml	HNO_3 conc.	&	30 ml	HNO_3 conc.
10 ml	HF (43%)		20 ml	HF (48%)
60 ml	H_2O		50 ml	H_2O

These two etchants reacted in a similar manner as Tuckers Reagent (as could be expected given their similar compositions).

(6)

15 g	$CuSO_4$	}
15 ml	HCl conc.	} Swab for 20-30 secs
90 ml	H_2O	}

Individual grains were not as well defined by this solution as they were with Poultons Etch. It also seemed to lose potency if not freshly prepared.

(7)

25 g	$CuCl_2$	} Swab then clean
200 ml	H_2O	} with HNO_3 conc.

This easy to prepare and handle etch, reacted very rapidly producing results equal to those achieved by any other solution. The only detrimental feature of this reactant was that fumes generated during cleaning in HNO_3 were exceedingly obnoxious. This etchant worked noticeably better when freshly prepared.

(8)

35 g	$FeCl_3$	}	Swab - rinse in running
200 ml	H_2O	}	then immerse in HNO_3

This iron-chloride based solution is easy to prepare and handle, it also causes no major problems when used in direct contact with skin. The etched surfaces produced following immersion were very similar to those achieved by Poultons or $CuCl_2$ solutions. However, the inherent problems associated with these alternatives were not encountered. This solution was used extensively to reveal the grain structure of the samples investigated during the current research.

Appendix H

Final Sample OES Composition Results

	SAMPLE	Silicon	Iron	Copper	Magnesium	Zinc	Nickel	Manganese	Lead	Chromium	Titanium	Tin	Calcium	Sodium	Vanadium	Gallium	Boron	Lithium	Berillium	Bismuth	Zirconium	Strontium
	#	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
1	37-1-2.	10.056	0.183	0.0007	0.0023	0	0.0004	0.0377	0	0	0.0056	0	0.0002	0.0004	0.0022	0.0098	0.0003	0	0.0001	0	0.0002	0.0214
2	43-2-2.	9.983	0.181	0.0007	0.1201	0	0.0002	0.0379	0	0	0.0053	0	0.0001	0.0003	0.0019	0.0098	0.0003	0	0	0	0.0002	0.0133
3	44-3-2.	9.6425	0.686	0.001	0.0915	0	0.0007	0.0387	0	0	0.0053	0	0.0001	0.0002	0.002	0.0102	0.0003	0	0	0	0.0002	0.0033
4	48-4-2.	9.8345	0.702	0.0009	0.085	0	0.0006	0.4644	0.0023	0	0.0051	0	0.0001	0	0.0019	0.0104	0.0004	0	0	0	0.0009	0.0011
5	61-1-3.	10.051	0.148	0.0019	0.0028	0	0.0005	0.0013	0.0005	0	0.0056	0	0.0003	0.0007	0.0023	0.0099	0.0003	0	0.0001	0	0.0002	0.0115
6	67-2-3.	9.9713	0.145	0.0021	0.0845	0	0.0002	0.0011	0	0	0.0054	0	0.0002	0.0001	0.0019	0.0097	0.0003	0	0	0	0.0001	0.0048
7	68-3-3.	9.8202	0.514	0.0025	0.0768	0	0.0007	0.0022	0.0003	0	0.0053	0	0.0001	0	0.0022	0.0102	0.0004	0	0	0	0.0002	0.0015
8	72-4-3.	9.5169	0.549	0.0027	0.069	0	0.0006	0.4387	0.0032	0	0.0051	0	0.0001	0	0.0022	0.0104	0.0004	0	0	0	0.0009	0
9	1-1-4.	9.9834	0.14	0.0007	0.0024	0	0.0003	0.0044	0	0	0.0054	0	0.0001	0.0155	0.0022	0.0101	0.0003	0	0.0001	0	0.0001	0
10	7-2-4.	10.045	0.135	0.0007	0.0537	0	0.0001	0.0046	0	0	0.0051	0	0.0001	0.0228	0.002	0.0104	0.0002	0	0	0	0.0001	0
11	8-3-4.	9.8072	0.598	0.0009	0.0377	0.0005	0.0008	0.0056	0.0001	0	0.0053	0	0.0001	0.008	0.0023	0.0107	0.0006	0	0	0	0.0002	0
12	12-4-4.	9.531	0.606	0.001	0.0265	0.0007	0.0007	0.578	0.0039	0	0.0051	0	0	0.0037	0.0021	0.0108	0.0005	0	0	0	0.0012	0
13	109-1-5.	13.067	0.173	0.0007	0.0042	0	0.0002	0.0015	0	0	0.0078	0	0.0025	0.0001	0.0027	0.0092	0.0001	0	0	0	0.0002	0.0207
14	120-2-5.	12.636	0.713	0.0009	0.1173	0	0.0007	0.4424	0.0015	0	0.0073	0.0002	0.0021	0.0001	0.0027	0.0103	0.0004	0	0	0	0.0009	0.0199
15	97-1-6.	12.914	0.181	0.0017	0.004	0	0.0003	0.0069	0	0	0.0078	0	0.0019	0.0001	0.0027	0.0092	0.0003	0	0	0	0.0002	0.0154
16	108-2-6.	12.64	0.838	0.0022	0.1289	0.0004	0.0009	0.4786	0.0022	0	0.0075	0.0001	0.0016	0.0001	0.0028	0.0106	0.0005	0	0	0	0.0011	0.0145
17	169-1-7.	11.27	0.156	0.0006	0.0022	0	0.0002	0.0014	0	0	0.0066	0	0.0001	0.0001	0.0024	0.0092	0.0002	0	0	0	0.0002	0
18	170-2-7.	11.302	0.157	0.0007	0.0012	0	0.0002	0.0016	0.0007	0	0.0066	0	0.0001	0.0032	0.0026	0.0098	0.0044	0	0	0	0.0002	0
19	171-3-7.	11.645	0.158	0.0007	0.0005	0	0.0004	0.0018	0.0009	0	0.0067	0	0	0.0034	0.0028	0.0098	0.0002	0	0	0	0.0002	0
20	172-4-7.	11.333	0.158	0.0007	0.0003	0	0.0003	0.0019	0.0013	0	0.0065	0	0.0001	0.0116	0.0028	0.0102	0.0002	0	0	0	0.0002	0
21	188-1-8.	11.136	0.669	0.0022	0.1015	0.0002	0.0008	0.4636	0.0018	0	0.0062	0	0.0001	0.0114	0.0025	0.0112	0.0004	0	0	0	0.0009	0
22	189-2-8.	10.852	0.645	0.0022	0.0813	0.0004	0.0005	0.4952	0.0019	0	0.006	0	0.0001	0.0242	0.0025	0.0112	0.0004	0	0	0	0.0009	0
23	190-3-8.	11.102	0.612	0.0022	0.0622	0.0005	0.0005	0.5144	0.002	0	0.0058	0	0.0001	0.0351	0.0024	0.0117	0.0006	0	0	0.0005	0.0008	0
24	191-4-8.	10.993	0.606	0.0023	0.0442	0.0007	0.0002	0.5377	0.002	0	0.0056	0	0.0001	0.0483	0.0026	0.0122	0.0004	0	0	0.0004	0.0007	0
25	180-1-9.	11.397	0.156	0.0007	0.0026	0	0.0002	0.002	0	0	0.0067	0	0.0001	0.0001	0.0024	0.0094	0.0007	0	0	0	0.0002	0.0139
26	181-2-9.	11.277	0.158	0.0006	0.0021	0	0.0002	0.002	0	0	0.0068	0	0	0	0.0026	0.0094	0.0002	0	0	0	0.0002	0.0091
27	182-3-9.	11.432	0.159	0.0007	0.0018	0.0001	0.0003	0.0021	0	0	0.0067	0	0	0.0001	0.0025	0.0093	0.0002	0	0	0	0.0002	0.009
28	183-4-9.	11.213	0.159	0.0007	0.0016	0.0005	0.0003	0.0022	0	0	0.0067	0	0	0	0.0029	0.0097	0.0002	0	0	0	0.0002	0.0149
29	204-1-10.	11.512	0.158	0.0007	0.0026	0.0008	0.0003	0.0013	0	0	0.1155	0	0.0001	0	0.0025	0.0127	0.0001	0	0.0001	0	0.0002	0.0045
30	205-2-10.	11.319	0.157	0.0008	0.0021	0.0024	0.0002	0.0014	0	0	0.2349	0	0	0	0.0025	0.0169	0	0	0.0001	0	0.0002	0
31	1-1-11.	9.7779	0.15	0.0004	0.0004	0	0	0.0009	0.0003	0.0003	0.0058	0	0.0001	0.0066	0.0014	0.0098	0.0001	0	0	0	0	0
32	7-2-11.	9.7839	0.154	0.0004	0.0797	0	0	0.0012	0.0002	0.0004	0.0053	0	0.0004	0.0071	0.0011	0.0096	0.0003	0	0	0	0.0001	0
33	9-3-11.	10.067	0.2	0.0004	0.0549	0	0	0.2445	0.0022	0.0006	0.0055	0	0.0002	0.0035	0.0012	0.01	0.0002	0	0	0	0.0004	0
34	11-4-11.	10.379	0.223	0.0006	0.0373	0	0.0001	0.6155	0.0052	0.0008	0.0056	0	0.0002	0.0045	0.0012	0.01	0	0	0	0	0.0009	0
35	2-1-12.	9.5065	0.621	0.0007	0.0011	0	0.0004	0.0038	0	0.0001	0.0055	0	0.0001	0.0076	0.0014	0.01	0.0003	0	0	0	0.0001	0
36	4-2-12.	9.4671	0.649	0.0006	0.0006	0	0.0003	0.2162	0.0004	0.0004	0.0055	0	0.0001	0.0013	0.0012	0.0099	0.0004	0	0	0	0.0003	0
37	6-3-12.	9.6771	0.682	0.0007	0.0004	0	0.0004	0.5267	0.003	0.0008	0.0055	0	0.0002	0.0017	0.0013	0.0107	0.0005	0	0	0	0.0008	0
38	12-4-12.	10.095	0.754	0.0009	0.0676	0	0.0004	0.5228	0.003	0.001	0.0056	0	0.0002	0.0029	0.0012	0.0103	0.0006	0	0	0	0.0008	0
39	3-1-13.	9.707	0.172	0.0004	0.0007	0	0	0.2012	0	0.0003	0.0056	0	0	0.003	0.0013	0.0096	0.0003	0	0	0	0.0003	0
40	5-2-13.	9.8561	0.211	0.0005	0.0001	0	0	0.5894	0.0024	0.0006	0.006	0	0.0001	0.0008	0.0013	0.0097	0.0004	0	0	0	0.0009	0
41	8-1-14.	9.6143	0.633	0.0005	0.0605	0	0.0003	0.0047	0.006	0	0.0056	0	0.0002	0.0028	0.0015	0.0102	0.0003	0	0	0	0	0
42	10-2-14.	9.8201	0.665	0.0007	0.033	0	0.0004	0.177	0.0058	0.0001	0.0058	0.0005	0.0004	0.0017	0.0014	0.01	0.0003	0	0	0	0.0003	0

	SAMPLE	Silicon	Iron	Copper	Magnesium	Zinc	Nickel	Manganese	Lead	Chromium	Titanium	Tin	Calcium	Sodium	Vanadium	Gallium	Boron	Lithium	Berillium	Bismuth	Zirconium	Strontium
	#	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
43	37-1-15.	9.5434	0.146	0.0003	0.0025	0	0	0.0014	0	0	0.0057	0	0.0001	0.0003	0.0013	0.0091	0.0001	0	0	0	0.0001	0
44	43-2-15.	9.7005	0.146	0.0004	0.0649	0	0	0.0018	0	0	0.0056	0	0.0002	0.0005	0.0012	0.0092	0.0003	0	0	0	0	0.0032
45	45-3-15.	9.9403	0.156	0.0005	0.0514	0	0	0.1831	0.0001	0	0.0058	0	0.0002	0.0007	0.0014	0.0094	0.0001	0	0	0	0.0003	0.0017
46	47-4-15.	10.312	0.163	0.0005	0.0217	0.0001	0.0001	0.474	0.0028	0	0.006	0	0.0002	0.0008	0.0014	0.0098	0.0003	0	0	0	0.0008	0
47	38-1-16.	9.4455	0.611	0.0006	0.0039	0	0.0004	0.0023	0.0005	0	0.0057	0	0.0001	0.0006	0.0015	0.0098	0.0003	0	0	0	0.0001	0.0005
48	40-2-16.	9.5422	0.608	0.0006	0.0033	0	0.0003	0.2159	0.0022	0	0.0056	0	0.0002	0.0008	0.0014	0.0099	0.0004	0	0	0	0.0003	0
49	42-3-16.	9.6747	0.608	0.0005	0.0026	0	0.0004	0.4625	0.0041	0	0.0056	0	0.0002	0.0007	0.0013	0.01	0.0006	0	0	0	0.0007	0
50	48-4-16.	10.068	0.616	0.0008	0.0371	0	0.0005	0.4647	0.0042	0	0.0059	0	0.0003	0.0009	0.0014	0.0101	0.0004	0	0	0	0.0007	0.0009
51	39-1-17.	9.7182	0.14	0.0003	0.0024	0	0	0.1835	0.0031	0	0.0057	0	0.0003	0.0018	0.0014	0.0095	0.0003	0	0	0	0.0003	0.0006
52	41-2-17.	10.103	0.147	0.0005	0.0018	0	0	0.4752	0.0056	0	0.0059	0	0.0003	0.0017	0.0014	0.0097	0.0006	0	0	0	0.0007	0.0001
53	44-1-18.	9.5471	0.547	0.0005	0.0546	0	0.0002	0.0026	0	0	0.0057	0	0.0003	0.0022	0.0014	0.0098	0.0003	0	0	0	0	0.0011
54	46-2-18.	9.9149	0.562	0.0006	0.0296	0	0.0004	0.2003	0.0007	0	0.0057	0	0.0004	0.0024	0.0015	0.0102	0.0003	0	0	0	0.0004	0.0006
55	73-1-19.	12.689	0.173	0.0006	0.0028	0	0	0.0017	0	0	0.0076	0	0.0009	0.0141	0.0021	0.0097	0	0	0	0	0.0001	0.0003
56	79-2-19.	12.933	0.184	0.0007	0.078	0	0	0.0023	0	0	0.0077	0	0.0009	0.0117	0.0021	0.01	0	0	0	0	0.0001	0.0002
57	81-3-19.	13.193	0.185	0.0007	0.0544	0	0	0.2005	0.0004	0	0.0081	0	0.0006	0.0057	0.0022	0.0096	0.0001	0	0	0	0.0004	0
58	83-4-19.	13.6	0.191	0.0009	0.0431	0.0001	0.0002	0.4901	0.003	0.0003	0.0083	0	0.0008	0.0104	0.0025	0.0101	0.0002	0	0	0	0.0008	0
59	74-1-20.	12.595	0.671	0.0007	0.0037	0	0.0003	0.0029	0	0.0002	0.0079	0	0.0007	0.0112	0.0023	0.01	0.0004	0	0	0	0.0002	0
60	76-2-20.	12.559	0.682	0.0008	0.0026	0	0.0004	0.1915	0	0.0003	0.0081	0	0.0004	0.0022	0.0022	0.0099	0.0003	0	0	0	0.0004	0
61	78-3-20.	12.792	0.698	0.0009	0.0022	0	0.0005	0.4304	0.0016	0.0006	0.0082	0	0.0003	0.0022	0.0022	0.0101	0.0003	0	0	0	0.0007	0
62	84-4-20.	13.142	0.705	0.001	0.0472	0	0.0006	0.4176	0.0018	0.0009	0.0086	0	0.0004	0.0043	0.0024	0.0103	0.0003	0	0	0	0.0008	0
63	75-1-21.	12.591	0.192	0.0006	0.0021	0	0	0.1647	0	0	0.0076	0.0002	0.0003	0.0037	0.0022	0.0095	0.0001	0	0	0	0.0003	0
64	77-2-21.	13.072	0.215	0.0008	0.0017	0	0.0001	0.4398	0.0019	0.0001	0.008	0	0.0004	0.0028	0.0024	0.0098	0.0004	0	0	0	0.0007	0
65	80-1-22.	12.154	0.709	0.0007	0.0626	0	0.0003	0.0036	0	0.0001	0.0082	0	0.0006	0.0037	0.0021	0.0098	0.0001	0	0	0	0.0001	0
66	82-2-22.	12.801	0.722	0.0009	0.0393	0	0.0004	0.1753	0	0.0006	0.0086	0	0.0006	0.0028	0.0023	0.01	0.0002	0	0	0	0.0003	0
67	110-1-23.	12.603	0.664	0.0007	0.0033	0	0.0003	0.0027	0	0	0.008	0	0.0006	0.0023	0.0022	0.0099	0.0002	0	0	0	0.0002	0.0084
68	112-2-23.	12.58	0.654	0.0008	0.0031	0	0.0003	0.1983	0	0	0.008	0	0.0005	0.0024	0.0022	0.0097	0.0003	0	0	0	0.0004	0.0036
69	114-3-23.	12.802	0.669	0.0009	0.0031	0	0.0005	0.4442	0.002	0.0002	0.0082	0	0.0005	0.0026	0.0023	0.01	0.0003	0	0	0	0.0008	0.0045
70	120-4-23.	13.036	0.658	0.0011	0.0473	0	0.0006	0.4318	0.0019	0.0003	0.0085	0	0.0005	0.0026	0.0024	0.0101	0.0003	0	0	0	0.0008	0.0027
71	10-1-24.	9.7238	0.626	0.0008	0.1002	0	0.0006	0.198	0.0008	0	0.0081	0	0.0005	0.0146	0.0022	0.0079	0	0	0	0	0.0002	0
72	12-2-24.	9.654	0.647	0.0008	0.0822	0	0.0007	0.5116	0.001	0	0.0084	0	0.0005	0.0093	0.0024	0.0085	0	0	0	0	0.0001	0
73	118-1-25.	9.7574	0.581	0.0007	0.1045	0	0.0004	0.2105	0	0.0002	0.008	0	0.0006	0.0001	0.0025	0.0088	0.0001	0	0	0	0.0007	0.0262
74	120-2-25.	9.6658	0.582	0.0009	0.0761	0	0.0005	0.529	0	0.0002	0.0081	0	0.0006	0.0002	0.003	0.0095	0.0001	0	0	0	0.0008	0.0293
75	79-1-26.	13.496	0.174	0.0012	0.0983	0	0.0017	0.0038	0	0.0005	0.0079	0.0005	0.0004	0.0106	0.0034	0.0073	0	0	0	0	0	0
76	81-2-26.	13.545	0.182	0.0013	0.086	0	0.0018	0.2114	0.0004	0.0006	0.008	0.0006	0.0008	0.0078	0.0035	0.0074	0	0	0	0	0	0
77	83-3-26.	13.708	0.185	0.0014	0.0887	0	0.0017	0.4874	0.0007	0.0008	0.0081	0.0007	0.0008	0.0083	0.0035	0.0073	0	0	0	0	0	0
78	84-4-26.	14.002	0.513	0.0018	0.0808	0	0.0021	0.4742	0.0008	0.0011	0.0083	0.0008	0.0009	0.0068	0.0037	0.0076	0	0	0	0	0	0
79	159-1-27.	11.764	0.157	0.0008	0.0965	0	0.0016	0.2074	0.0004	0	0.0066	0.0007	0.0009	0.003	0.0032	0.0075	0	0	0	0	0	0.0191
80	195-2-27.	11.515	0.674	0.001	0.0995	0	0.002	0.4716	0.0008	0.0002	0.0065	0.001	0.0008	0.0029	0.0032	0.0079	0.0001	0	0	0	0	0.0256
81	4-1-28.	10.01	0.611	0.0008	0.0023	0	0.002	0.1948	0.0002	0.0001	0.0055	0.0008	0.0006	0.0149	0.0028	0.0082	0.0001	0	0	0	0	0
82	12-2-28.	9.9993	0.606	0.0009	0.0791	0	0.002	0.4476	0.0005	0.0002	0.0053	0.0009	0.0008	0.0106	0.0028	0.0084	0.0001	0	0	0	0	0
83	157-1-29.	11.575	0.157	0.0007	0.0052	0	0.0016	0.2098	0.0003	0	0.0063	0.0006	0.0006	0.0023	0.0031	0.0075	0	0	0	0	0	0.0269
84	160-2-29.	11.527	0.162	0.0007	0.0046	0	0.0015	0.2099	0.0003	0.0001	0.0064	0.0006	0.0007	0.0029	0.0031	0.0072	0	0	0	0	0	0.0205
85	77-1-30.	12.944	0.173	0.0009	0.0019	0	0.0016	0.4669	0.0002	0.0004	0.0071	0.0006	0.001	0.01	0.0033	0.0074	0	0	0	0	0	0.0005
86	84-2-30.	13.154	0.516	0.0011	0.1285	0	0.0017	0.4471	0.0003	0.0007	0.007	0.0007	0.0016	0.0135	0.0034	0.0077	0	0	0	0	0	0.0009
87	109-1-31.	12.933	0.175	0.0009	0.0027	0	0.0016	0.0044	0.0003	0.0002	0.0073	0.0005	0.0005	0.0013	0.0033	0.0071	0	0	0	0	0	0.0227
88	115-2-31.	13.055	0.173	0.011	0.0942	0.0126	0.0016	0.0045	0.0003	0.0002	0.0074	0.0005	0.0007	0.0021	0.0033	0.007	0	0	0	0	0	0.0246
89	117-3-31.	13.096	0.182	0.001	0.1006	0	0.0017	0.1833	0.0006	0.0003	0.0074	0.0006	0.0012	0.0026	0.0033	0.0073	0	0	0	0	0	0.0263
90	120-4-31.	13.247	0.189	0.0011	0.11	0	0.0017	0.3876	0.0009	0.0003	0.0075	0.0006	0.001	0.0025	0.0033	0.0074	0	0	0	0	0	0.0216
91	38-1-32.	10.02	0.615	0.0008	0.0035	0	0.0019	0.0019	0	0.0002	0.0053	0.0008	0.0002	0.0002	0.0029	0.0079	0	0	0	0	0	0.0206

	SAMPLE	Silicon	Iron	Copper	Magnesium	Zinc	Nickel	Manganese	Lead	Chromium	Titanium	Tin	Calcium	Sodium	Vanadium	Gallium	Boron	Lithium	Berillium	Bismuth	Zirconium	Strontium
	#	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
92	40-2-32.	10.023	0.639	0.0008	0.0037	0	0.002	0.1983	0.0002	0.0002	0.0053	0.0008	0.0004	0.002	0.0029	0.0079	0	0	0	0	0	0.0212
93	46-3-32.	10.257	0.427	0.0009	0.0859	0	0.0019	0.1951	0.0002	0.0002	0.0053	0.0008	0.0009	0.0038	0.0029	0.008	0	0	0	0	0	0.021
94	48-4-32.	10.159	0.628	0.0009	0.077	0	0.002	0.4351	0.0006	0.0002	0.0052	0.0009	0.001	0.0036	0.0029	0.0081	0	0	0	0	0	0.0197
95	1-1-33.	10.234	0.143	0.0006	0.0024	0	0.0016	0.0043	0	0	0.0053	0.0005	0.0008	0.0132	0.0027	0.0078	0	0	0	0	0	0.0003
96	2-2-33.	10.261	0.62	0.0008	0.0017	0	0.0019	0.005	0	0.0002	0.0052	0.0006	0.0009	0.0192	0.0028	0.0081	0	0	0	0	0	0.0004
97	6-3-33.	10.24	0.635	0.0009	0.0011	0	0.0019	0.4718	0.0004	0.0003	0.0051	0.0009	0.0009	0.0148	0.0028	0.0083	0	0	0	0	0	0.0004
98	12-4-33.	10.393	0.622	0.0009	0.0786	0	0.0019	0.4629	0.0004	0.0003	0.0052	0.0008	0.0016	0.0168	0.0028	0.0086	0	0	0	0	0	0.0007
99	3-1-34.	10.183	0.141	0.0006	0.0013	0	0.0016	0.1939	0	0	0.0054	0.0007	0.0006	0.0121	0.0029	0.0081	0	0	0	0	0	0.0002
100	5-2-34.	10.165	0.144	0.0006	0.0006	0	0.0016	0.4775	0.0004	0	0.0053	0.0008	0.0008	0.0107	0.0029	0.0082	0	0	0	0	0	0.0003
101	7-1-35.	10.222	0.136	0.0006	0.1041	0	0.0016	0.0034	0.0002	0	0.0055	0.0005	0.0006	0.0197	0.0029	0.0083	0	0	0	0	0	0.0008
102	9-2-35.	10.337	0.139	0.0007	0.1035	0	0.0016	0.2102	0.0006	0	0.0055	0.0006	0.0009	0.0214	0.0028	0.0085	0	0	0	0	0	0.001
103	8-1-36.	10.281	0.568	0.0008	0.1086	0	0.0019	0.0038	0	0.0001	0.0054	0.0007	0.0007	0.0214	0.003	0.0087	0	0	0	0	0	0.0003
104	24-2-36.	10.231	0.58	0.0008	0.0944	0	0.0019	0.5252	0.001	0.0002	0.0875	0.001	0.0009	0.0157	0.0029	0.0097	0	0	0	0	0	0.0005
105	11-1-37.	10.344	0.143	0.0006	0.1097	0	0.0015	0.5324	0.0009	0	0.0056	0.0007	0.0008	0.018	0.003	0.0086	0	0	0	0	0	0.0003
106	35-2-37.	10.589	0.142	0.0007	0.1023	0	0.0015	0.5217	0.0011	0	0.1651	0.0009	0.0008	0.014	0.0029	0.0107	0	0	0	0	0	0.0004
107	123-1-38.	12.926	0.171	0.0009	0.0018	0	0.0016	0.2124	0.0001	0.0002	0.0931	0.0007	0.0008	0.0024	0.0034	0.0083	0	0	0	0	0	0.0291
108	135-2-38.	13.111	0.172	0.0009	0.0013	0	0.0016	0.2107	0.0003	0.0003	0.1804	0.0008	0.0007	0.0027	0.0035	0.0095	0	0	0	0	0	0.0222
109	143-3-38.	13.19	0.174	0.0011	0.1158	0	0.0017	0.4963	0.0007	0.0003	0.1739	0.0009	0.0009	0.0031	0.0035	0.0096	0	0	0	0	0	0.0268
110	144-4-38.	13.256	0.806	0.0013	0.1104	0	0.002	0.4817	0.0008	0.0007	0.1685	0.0011	0.0009	0.0029	0.0036	0.0098	0	0	0	0	0.0001	0.0295
111	37-1-39.	10.342	0.143	0.0006	0.0023	0	0.0016	0.0033	0.0003	0	0.0055	0.0007	0.0003	0.0018	0.003	0.0081	0	0	0	0	0	0.0306
112	39-2-39.	10.272	0.145	0.0006	0.0024	0	0.0017	0.2299	0.0006	0	0.0055	0.0008	0.0004	0.0026	0.0029	0.0083	0	0	0	0	0	0.0263
113	41-3-39.	10.199	0.147	0.0006	0.0021	0	0.0017	0.5556	0.0011	0	0.0054	0.0009	0.0005	0.0025	0.0029	0.0082	0	0	0	0	0	0.0251
114	42-4-39.	10.351	0.742	0.0009	0.0021	0	0.002	0.5397	0.0011	0.0003	0.0055	0.0011	0.0005	0.0029	0.0031	0.0085	0	0	0	0	0	0.0225
115	43-1-40.	10.356	0.139	0.0006	0.0979	0	0.0015	0.0031	0.0001	0	0.0055	0.0007	0.0005	0.0027	0.003	0.0081	0	0	0	0	0	0.0219
116	44-2-40.	10.327	0.478	0.0008	0.1057	0	0.0018	0.0038	0.0002	0.0001	0.0055	0.0007	0.0005	0.0026	0.003	0.0083	0	0	0	0	0	0.0253
117	45-1-41.	10.27	0.14	0.0008	0.0983	0	0.0016	0.1699	0.0001	0	0.0055	0.0007	0.0006	0.003	0.0029	0.0081	0	0	0	0	0	0.0261
118	47-2-41.	10.307	0.147	0.0006	0.0942	0	0.0016	0.4739	0.0006	0	0.0054	0.0008	0.0005	0.0038	0.003	0.0083	0	0	0	0	0	0.0191
119	74-1-42.	13.168	0.593	0.0011	0.0024	0	0.0017	0.0041	0	0.0003	0.0071	0.0006	0.0009	0.0131	0.0035	0.0077	0	0	0	0	0	0.0006
120	76-2-42.	12.99	0.583	0.0011	0.002	0	0.0019	0.2205	0.0001	0.0003	0.007	0.0007	0.0011	0.0185	0.0035	0.0079	0	0	0	0	0	0.001
121	78-3-42.	13.178	0.584	0.0012	0.0021	0	0.0018	0.5142	0.0005	0.0004	0.0071	0.0008	0.0012	0.0184	0.0035	0.008	0	0	0	0	0	0.0011
122	84-4-42.	13.416	0.575	0.0012	0.1421	0	0.0019	0.5005	0.0006	0.0005	0.0072	0.0008	0.0012	0.0204	0.0035	0.0081	0	0	0	0	0	0.0012
123	75-1-43.	12.667	0.163	0.0008	0.0024	0	0.0016	0.1964	0	0	0.0067	0.0006	0.0012	0.0208	0.0032	0.0077	0	0	0	0	0	0.0009
124	81-2-43.	13.191	0.173	0.0009	0.0855	0	0.0015	0.1983	0	0.0002	0.0072	0.0006	0.0015	0.0114	0.0034	0.0075	0	0	0	0	0	0.0006
125	79-1-44.	12.522	0.164	0.0008	0.0963	0	0.0015	0.0046	0	0	0.0068	0.0005	0.0015	0.0177	0.0032	0.0074	0	0	0	0	0	0.0006
126	80-2-44.	12.463	0.564	0.001	0.0866	0	0.0019	0.0054	0	0.0002	0.0069	0.0006	0.0014	0.0139	0.0032	0.0075	0	0	0	0	0	0.0005
127	82-1-45.	12.729	0.627	0.001	0.0989	0	0.0019	0.1878	0	0.0004	0.007	0.0008	0.0003	0.0118	0.0034	0.0078	0	0	0	0	0	0
128	94-2-45.	12.795	0.619	0.001	0.0949	0	0.002	0.1843	0.0001	0.0005	0.0758	0.0008	0.0005	0.0092	0.0034	0.0085	0	0	0	0	0	0
129	83-1-46.	12.571	0.17	0.0008	0.0942	0	0.0017	0.5559	0.0005	0.0002	0.0073	0.0007	0.0005	0.0135	0.0032	0.0074	0	0	0	0	0	0
130	95-2-46.	12.642	0.169	0.0009	0.0934	0	0.0017	0.5431	0.0005	0.0003	0.0751	0.0008	0.0004	0.0125	0.0032	0.0083	0	0	0	0	0	0
131	110-1-47.	12.66	0.612	0.0011	0.0028	0	0.0021	0.0045	0	0.0005	0.0075	0.0008	0.0008	0.0017	0.0034	0.0073	0	0	0	0	0	0.0276
132	112-2-47.	12.633	0.61	0.0011	0.0022	0.0002	0.0021	0.1953	0.0003	0.0005	0.0074	0.0008	0.0005	0.0022	0.0033	0.0074	0	0	0	0	0	0.0271
133	114-3-47.	12.824	0.624	0.0011	0.0018	0.0015	0.002	0.5028	0.0007	0.0006	0.0076	0.0009	0.0005	0.002	0.0034	0.0073	0	0	0	0	0	0.0268
134	120-4-47.	12.918	0.604	0.0012	0.1161	0.0011	0.0021	0.4865	0.0007	0.0006	0.0075	0.0009	0.0007	0.0022	0.0034	0.0077	0	0	0	0	0	0.031
135	111-1-48.	12.911	0.173	0.0009	0.0028	0	0.0017	0.1928	0.0002	0.0003	0.0075	0.0007	0.0006	0.0016	0.0033	0.0072	0	0	0	0	0	0.0275
136	113-2-48.	12.982	0.179	0.001	0.0018	0	0.0017	0.4814	0.0006	0.0003	0.0075	0.0008	0.0005	0.0017	0.0034	0.0073	0	0	0	0	0	0.024
137	116-1-49.	12.844	0.636	0.0011	0.102	0	0.002	0.0046	0	0.0005	0.0074	0.0008	0.0006	0.0015	0.0034	0.0075	0	0	0	0	0	0.0268
138	118-2-49.	12.918	0.648	0.0011	0.1173	0	0.002	0.1761	0.0001	0.0005	0.0075	0.0008	0.0006	0.0016	0.0034	0.0075	0	0	0	0	0	0.0234
139	145-1-50.	11.419	0.15	0.0007	0.0022	0	0.0016	0.165	0.0021	0	0.0062	0.0006	0.0003	0.0173	0.0031	0.0078	0	0	0	0	0	0.0006
140	147-2-50.	11.517	0.145	0.0008	0.1215	0	0.0017	0.1584	0.0022	0	0.0061	0.0006	0.0007	0.029	0.003	0.0081	0	0	0	0	0	0.0003

	SAMPLE	Silicon	Iron	Copper	Magnesium	Zinc	Nickel	Manganese	Lead	Chromium	Titanium	Tin	Calcium	Sodium	Vanadium	Gallium	Boron	Lithium	Berillium	Bismuth	Zirconium	Strontium
	#	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
141	151-1-51.	11.384	0.146	0.0008	0.1047	0	0.0016	0.1436	0.0001	0	0.0999	0.0007	0.0002	0.0147	0.0031	0.0091	0	0	0	0	0	0.0001
142	155-2-51.	11.375	0.143	0.0008	0.1099	0	0.0017	0.1391	0.0001	0	0.1832	0.0007	0.0006	0.0214	0.003	0.0102	0	0	0	0	0	0.0003
143	158-1-52.	11.188	0.626	0.0009	0.003	0	0.002	0.1904	0.0005	0.0003	0.007	0.001	0.0005	0.0026	0.0032	0.0079	0	0	0	0	0	0.0284
144	160-2-52.	11.273	0.611	0.0009	0.1162	0	0.002	0.1862	0.0005	0.0003	0.007	0.0009	0.0003	0.0022	0.0032	0.0079	0	0	0	0	0	0.0255
145	164-1-53.	11.281	0.607	0.0013	0.1109	0.0009	0.0026	0.1909	0.001	0.0004	0.0986	0.0013	0.0006	0.0024	0.0034	0.0093	0	0	0	0	0	0.0308
146	168-2-53.	11.341	0.561	0.001	0.1022	0	0.002	0.1783	0.0005	0.0003	0.1841	0.001	0.0002	0.0015	0.0032	0.0103	0	0	0	0	0	0.0269
147	149-1-54.	11.527	0.167	0.0009	0.0021	0.0002	0.0005	0.2028	0.0008	0	0.1053	0	0.0002	0.0104	0.0025	0.0133	0.0002	0	0.0001	0.0007	0.0004	0
148	150-2-54.	11.438	0.555	0.0001	0.0016	0	0.0021	0.192	0.0002	0.0005	0.0965	0.0009	0.0002	0.0112	0.0033	0.0095	0	0	0	0	0	0.0002
149	165-1-55.	11.748	0.165	0.0008	0.0021	0.002	0.0006	0.2039	0.0016	0	0.2307	0.0002	0.0002	0.0009	0.0026	0.0161	0.0002	0	0.0001	0.0012	0.0005	0.0241
150	166-2-55.	11.492	0.637	0.001	0.0014	0.0024	0.0009	0.1995	0.0016	0	0.2206	0.0004	0.0002	0.0014	0.0026	0.0163	0.0003	0	0.0001	0.0012	0.0005	0.0296
151	163-1-56.	11.588	0.163	0.0008	0.116	0.0004	0.0004	0.2169	0.0011	0	0.1157	0	0.0003	0.0016	0.0026	0.0129	0.0002	0	0.0001	0.0002	0.0005	0.0294
152	167-2-56.	11.621	0.163	0.0009	0.1304	0.0018	0.0005	0.2155	0.0028	0	0.2265	0	0.0003	0.0017	0.0025	0.0158	0.0002	0	0.0001	0.0008	0.0005	0.0255
153	152-1-57.	11.263	0.589	0.001	0.1151	0.0006	0.0008	0.2146	0.0012	0	0.1017	0	0.0002	0.0188	0.0025	0.0137	0.0003	0	0.0001	0.0011	0.0004	0
154	156-2-57.	11.408	0.577	0.001	0.121	0.0021	0.0008	0.2174	0.0021	0	0.2088	0.0003	0.0006	0.0219	0.0026	0.0168	0.0003	0	0.0001	0.0019	0.0004	0
155	13-1-58.	10.045	0.143	0.0007	0.0039	0	0.0003	0.002	0	0	0.096	0	0.0003	0.0209	0.0019	0.0127	0.0001	0	0.0001	0.0008	0.0001	0
156	15-2-58.	10.323	0.152	0.0008	0.0032	0.0009	0.0008	0.2231	0.0012	0	0.0977	0	0.0003	0.02	0.0023	0.0135	0.0002	0	0.0001	0.0017	0.0005	0
157	17-3-58.	10.102	0.144	0.0007	0.0018	0	0.0017	0.5021	0.0006	0.0001	0.0887	0.0009	0.0004	0.0156	0.0029	0.0096	0	0	0	0	0	0.0002
158	23-4-58.	10.058	0.141	0.0006	0.1319	0	0.0016	0.4923	0.0006	0.0001	0.0876	0.0007	0.0002	0.0215	0.0028	0.0096	0	0	0	0	0	0.0001
159	19-1-59.	10.212	0.136	0.0006	0.1	0	0.0016	0.0054	0	0.0001	0.1004	0.0007	0	0.0165	0.003	0.0093	0	0	0	0	0	0
160	21-2-59.	10.414	0.152	0.0008	0.1329	0.0004	0.0006	0.2081	0.0009	0	0.1084	0	0.0002	0.0158	0.0023	0.0135	0.0002	0	0.0001	0.0011	0.0004	0
161	26-1-60.	9.9126	0.581	0.0007	0.0009	0	0.0019	0.0038	0	0.0003	0.1886	0.0008	0	0.0112	0.003	0.0105	0	0	0	0	0	0
162	28-2-60.	9.8783	0.58	0.0009	0.0008	0	0.0022	0.1937	0.0004	0.0004	0.1899	0.0011	0	0.0068	0.0031	0.0111	0	0	0	0	0	0
163	30-3-60.	9.9288	0.586	0.0009	0.0005	0	0.0021	0.4837	0.001	0.0006	0.1855	0.0012	0	0.0104	0.0031	0.0113	0	0	0	0	0	0
164	36-4-60.	9.9893	0.571	0.0009	0.1515	0	0.002	0.4723	0.0008	0.0007	0.1827	0.0011	0.0001	0.0117	0.0031	0.0112	0	0	0	0	0	0
165	68-1-61.	10.01	0.576	0.0008	0.1026	0	0.002	0.004	0.0002	0.0003	0.1853	0.0009	0.0001	0.0003	0.003	0.0104	0	0	0	0.0001	0	0.0244
166	70-2-61.	10.19	0.574	0.0009	0.1284	0	0.002	0.0404	0.0002	0.0003	0.2014	0.001	0.0001	0.0004	0.003	0.0107	0	0	0	0	0	0.0296
167	146-1-62.	11.181	0.616	0.0008	0.0015	0	0.002	0.1977	0	0.0002	0.0065	0.0008	0	0.0073	0.0032	0.0078	0	0	0	0	0	0
168	148-2-62.	11.41	0.617	0.0008	0.1141	0	0.0019	0.2334	0	0.0002	0.0065	0.0008	0	0.0108	0.0032	0.0079	0	0	0	0	0	0
169	153-1-63.	11.282	0.15	0.0007	0.0017	0	0.0016	0.1897	0.0001	0	0.1996	0.0008	0	0.0082	0.003	0.0102	0	0	0	0	0	0
170	154-2-63.	11.542	0.224	0.0008	0.001	0	0.0016	0.1872	0.0001	0.0001	0.1994	0.0008	0.0001	0.0105	0.0031	0.0102	0	0	0	0	0	0
171	161-1-64.	11.237	0.151	0.0007	0.002	0	0.0017	0.1963	0.0002	0	0.1101	0.0009	0	0.0002	0.0031	0.0089	0	0	0	0	0	0.0283
172	162-2-64.	11.357	0.575	0.0009	0.0016	0	0.002	0.1924	0.0002	0.0003	0.1088	0.001	0.0001	0.0005	0.0032	0.009	0	0	0	0	0	0.0261
173	147-1-65.	11.292	0.149	0.0006	0.1011	0	0.0016	0.1992	0	0	0.0066	0.0006	0	0.0117	0.003	0.0077	0	0	0	0	0	0
174	155-2-65.	11.483	0.149	0.0007	0.1129	0	0.0017	0.1943	0.0001	0	0.2019	0.0007	0.0002	0.013	0.0031	0.0103	0	0	0	0	0	0
175	32-1-66.	10.124	0.568	0.0008	0.1084	0	0.002	0.0048	0	0.0001	0.169	0.0008	0	0.0233	0.0028	0.0107	0	0	0	0	0	0
176	34-2-66.	10.13	0.573	0.0008	0.1197	0	0.002	0.1896	0.0002	0.0002	0.2053	0.0009	0.0002	0.0185	0.0028	0.0111	0	0	0	0	0	0
177	31-1-67.	10.184	0.135	0.0006	0.1037	0	0.0016	0.0038	0	0	0.1742	0.0006	0	0.0213	0.0028	0.0104	0	0	0	0	0	0
178	33-2-67.	10.045	0.135	0.0006	0.114	0	0.0017	0.1722	0.0002	0	0.2013	0.0008	0.0001	0.017	0.0027	0.0107	0	0	0	0	0	0
179	20-1-68.	9.9955	0.589	0.0008	0.0994	0	0.002	0.0036	0	0.0002	0.1008	0.0009	0	0.0098	0.0029	0.0093	0.0001	0	0	0	0	0
180	22-2-68.	10.133	0.598	0.0008	0.1279	0	0.002	0.189	0.0002	0.0002	0.1096	0.0009	0	0.0074	0.0029	0.0096	0	0	0	0	0	0
181	14-1-69.	10.152	0.443	0.0008	0.0024	0	0.0018	0.0053	0	0.0001	0.1042	0.0009	0	0.014	0.0029	0.0094	0	0	0	0	0	0
182	18-2-69.	10.13	0.45	0.0009	0.0015	0	0.002	0.4729	0.0006	0.0002	0.1015	0.0011	0	0.0142	0.0029	0.0096	0	0	0	0	0	0
183	25-1-70.	9.8298	0.135	0.0005	0.0013	0	0.0015	0.0029	0	0	0.0945	0.0007	0	0.0128	0.0027	0.009	0	0	0	0	0	0
184	27-2-70.	9.7786	0.131	0.0006	0.0007	0	0.0015	0.1703	0	0.0003	0.2329	0.0009	0.0001	0.014	0.0027	0.0111	0	0	0	0	0	0
185	29-3-70.	9.9225	0.138	0.0006	0.0002	0	0.0017	0.4804	0.0006	0.0004	0.2351	0.0009	0.0002	0.0105	0.0027	0.0113	0	0	0	0	0	0
186	35-4-70.	9.9084	0.135	0.0006	0.1197	0	0.0016	0.4641	0.0004	0.0004	0.2262	0.0009	0	0.0188	0.0027	0.0114	0	0	0	0	0	0
187	49-1-72.	9.7356	0.135	0.0005	0.002	0	0.0016	0.0044	0	0	0.1013	0.0008	0.0001	0.0008	0.0028	0.009	0	0	0	0	0	0.0294
188	51-2-72.	9.8437	0.139	0.0006	0.0016	0	0.0017	0.2095	0.0002	0.0001	0.0999	0.0009	0.0001	0.0009	0.0028	0.0092	0	0	0	0	0	0.0281
189	53-3-72.	9.7572	0.141	0.0006	0.0012	0	0.0018	0.5022	0.0006	0.0001	0.0982	0.001	0.0001	0.0009	0.0028	0.0092	0	0	0	0	0	0.0286

	SAMPLE	Silicon	Iron	Copper	Magnesium	Zinc	Nickel	Manganese	Lead	Chromium	Titanium	Tin	Calcium	Sodium	Vanadium	Gallium	Boron	Lithium	Berillium	Bismuth	Zirconium	Strontium
	#	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
190	59-4-72.	9.7237	0.14	0.0006	0.1122	0	0.0016	0.4904	0.0005	0.0001	0.0959	0.0009	0	0.0006	0.0028	0.0092	0	0	0	0	0	0.0299
191	55-1-73.	10.146	0.139	0.0008	0.0895	0	0.0016	0.0047	0	0	0.1038	0.0007	0	0.0009	0.0028	0.0092	0	0	0	0	0	0.0279
192	57-2-73.	10.189	0.141	0.0008	0.1219	0	0.0017	0.0669	0	0	0.103	0.0008	0.0001	0.0009	0.0029	0.0091	0	0	0	0	0	0.0299
193	50-1-74.	9.847	0.582	0.0007	0.0022	0	0.002	0.0039	0.0002	0.0002	0.0805	0.0009	0.0001	0.0006	0.0029	0.0091	0	0	0	0	0	0.0312
194	52-2-74.	9.7779	0.58	0.0008	0.0017	0	0.0021	0.1988	0.0005	0.0003	0.1116	0.001	0.0001	0.0008	0.0028	0.0097	0	0	0	0	0	0.0311
195	54-3-74.	9.69	0.583	0.0008	0.0012	0	0.002	0.4601	0.0008	0.0002	0.1101	0.0012	0.0001	0.0007	0.0028	0.0095	0	0	0	0	0	0.0268
196	60-4-74.	9.8624	0.572	0.0008	0.1176	0	0.002	0.4532	0.0008	0.0003	0.1085	0.0011	0	0.0007	0.0029	0.0097	0	0	0	0	0	0.0329
197	56-1-75.	10.061	0.58	0.0007	0.106	0	0.002	0.0042	0	0.0002	0.1026	0.0009	0	0.0008	0.0029	0.0093	0	0	0	0	0	0.0284
198	58-2-75.	10.117	0.58	0.0007	0.1391	0	0.002	0.028	0	0.0002	0.1012	0.0009	0.0002	0.0008	0.003	0.0094	0	0	0	0	0	0.0319
199	61-1-76.	10.268	0.149	0.0025	0.0016	0	0.0018	0.0027	0.0001	0.0003	0.1944	0.0009	0.0007	0.0011	0.0059	0.0121	0	0	0	0	0	0.028
200	63-2-76.	10.227	0.147	0.0025	0.0013	0	0.0017	0.213	0.0004	0.0004	0.189	0.0009	0.0001	0.0012	0.006	0.0122	0	0	0	0	0	0.0318
201	65-3-76.	10.677	0.161	0.0024	0.0018	0.0016	0.007	0.5106	0.004	0	0.2014	0	0.0001	0.0012	0.0057	0.0188	0.0002	0	0.0001	0.0005	0.0012	0.0336
202	71-4-76.	10.667	0.156	0.0024	0.1224	0.0012	0.004	0.5137	0.0036	0	0.1951	0	0.0001	0.0012	0.0056	0.0187	0.0005	0	0.0001	0.0001	0.001	0.0402
203	67-1-77.	10.511	0.149	0.0026	0.1128	0	0.0017	0.1669	0.0003	0.0003	0.1991	0.0009	0.0003	0.0013	0.0061	0.0123	0	0	0	0	0	0.0283
204	69-2-77.	10.926	0.161	0.0023	0.1238	0.0013	0.0004	0.1725	0.0008	0	0.2122	0	0.0002	0.0017	0.0058	0.0189	0.0001	0	0.0001	0.0001	0.0004	0.0318
205	62-1-78.	10.328	0.599	0.0028	0.0015	0	0.0021	0.004	0.0001	0.0006	0.1732	0.001	0.001	0.0013	0.0062	0.012	0	0	0	0	0	0.0282
206	64-2-78.	10.257	0.604	0.003	0.0015	0	0.0021	0.1888	0.0005	0.0007	0.197	0.0012	0.0002	0.0012	0.0063	0.0127	0	0	0	0	0	0.0303
207	66-3-78.	10.081	0.609	0.0029	0.0009	0	0.0021	0.4764	0.0008	0.0006	0.1935	0.0012	0.0001	0.0011	0.0061	0.0128	0	0	0	0	0	0.028
208	72-4-78.	10.344	0.594	0.003	0.1032	0	0.0021	0.4637	0.0007	0.0006	0.1948	0.0011	0.0018	0.002	0.0063	0.0127	0	0	0	0	0	0.0274
209	85-1-79.	13.045	0.175	0.0037	0.0011	0	0.0016	0.0063	0	0.0006	0.1023	0.0006	0	0.0162	0.0074	0.0107	0	0	0	0	0	0
210	87-2-79.	13.179	0.179	0.0038	0.0007	0	0.0016	0.2257	0.0001	0.0008	0.1016	0.0007	0.0004	0.0131	0.0074	0.0106	0	0	0	0	0	0
211	89-3-79.	13.164	0.183	0.0037	0.0001	0	0.0016	0.5232	0.0006	0.0008	0.0983	0.0007	0.0001	0.0132	0.0074	0.0107	0	0	0	0	0	0
212	95-4-79.	13.564	0.187	0.004	0.111	0	0.0017	0.5111	0.0005	0.0009	0.0994	0.0008	0.0006	0.0137	0.0074	0.0107	0	0	0	0	0	0
213	91-1-80.	13.454	0.177	0.0031	0.0965	0	0.0016	0.0066	0	0.0006	0.0367	0.0006	0.0011	0.0061	0.0072	0.0093	0	0	0	0	0	0
214	93-2-80.	13.206	0.182	0.0034	0.1006	0	0.0017	0.2066	0.0002	0.0006	0.155	0.0007	0	0.0072	0.0072	0.0112	0	0	0	0	0	0
215	86-1-81.	12.971	0.603	0.0041	0.0021	0	0.0019	0.0073	0	0.0008	0.1038	0.0007	0.0001	0.0176	0.0074	0.0108	0	0	0	0	0	0.0002
216	88-2-81.	13.102	0.636	0.0033	0.0024	0.0012	0.0009	0.1915	0.0008	0.0003	0.1124	0	0.0002	0.0123	0.0077	0.0169	0.0003	0	0.0001	0.0011	0.0006	0
217	90-3-81.	12.96	0.617	0.004	0.0011	0.0004	0.002	0.4504	0.0005	0.001	0.1015	0.0009	0.0002	0.0127	0.0075	0.0109	0	0	0	0	0	0.0001
218	96-4-81.	13.243	0.599	0.0045	0.0957	0.0004	0.002	0.4373	0.0005	0.0011	0.1004	0.0008	0.0007	0.0169	0.0075	0.011	0	0	0	0	0	0
219	92-1-82.	13.394	0.669	0.0036	0.0976	0	0.002	0.0066	0	0.0008	0.1032	0.0007	0.001	0.0209	0.0076	0.0109	0	0	0	0	0	0
220	94-2-82.	13.437	0.695	0.0037	0.1016	0	0.0021	0.1852	0.0001	0.0009	0.1043	0.0008	0.0014	0.0082	0.0075	0.0109	0	0	0	0	0.0001	0
221	97-1-83.	13.202	0.173	0.0037	0.0027	0	0.0016	0.0063	0	0.0006	0.1943	0.0007	0.0002	0.0172	0.0073	0.0119	0	0	0	0	0	0.0006
222	99-2-83.	12.963	0.173	0.0036	0.0018	0	0.0016	0.2127	0.0002	0.0006	0.1875	0.0007	0.0002	0.0142	0.0072	0.0117	0	0	0	0	0	0.0006
223	101-3-83.	13.18	0.179	0.004	0.0013	0	0.0017	0.551	0.0006	0.0007	0.1858	0.0009	0.0001	0.0186	0.0073	0.0119	0	0	0	0	0	0.0004
224	107-4-83.	13.087	0.177	0.0041	0.1454	0	0.0016	0.5313	0.0006	0.0008	0.177	0.0008	0	0.0198	0.0072	0.012	0	0	0	0	0	0.0001
225	103-1-84.	12.776	0.165	0.0031	0.1051	0	0.0016	0.0036	0	0.0003	0.2071	0.0006	0	0.0205	0.0073	0.0123	0	0	0	0	0	0.0006
226	105-2-84.	12.888	0.17	0.0033	0.1153	0	0.0016	0.1919	0.0001	0.0004	0.2055	0.0007	0	0.0151	0.0073	0.0122	0	0	0	0	0	0.0005
227	98-1-85.	12.882	0.593	0.0037	0.0017	0	0.0019	0.008	0	0.0008	0.1982	0.0008	0.0003	0.0189	0.0073	0.0121	0	0	0	0	0	0.0003
228	100-2-85.	12.913	0.593	0.0038	0.001	0	0.0019	0.2058	0.0002	0.0008	0.1951	0.0009	0.0004	0.0154	0.0072	0.012	0	0	0	0	0	0.0004
229	102-3-85.	12.893	0.59	0.0039	0.0005	0	0.002	0.5052	0.0006	0.0009	0.1913	0.001	0.0001	0.0152	0.0072	0.0121	0	0	0	0	0	0.0004
230	108-4-85.	13.104	0.564	0.0043	0.1358	0	0.002	0.4891	0.0006	0.001	0.1852	0.0009	0.0003	0.0217	0.0073	0.0123	0	0	0	0	0	0.0002
231	104-1-86.	13.158	0.596	0.0038	0.0997	0	0.0019	0.0075	0	0.0008	0.1966	0.0008	0.0006	0.0096	0.0073	0.0118	0	0	0	0	0	0.0002
232	106-2-86.	13.165	0.593	0.004	0.0925	0	0.002	0.1931	0.0002	0.0009	0.193	0.0009	0.0005	0.0126	0.0072	0.0118	0	0	0	0	0	0.0002
233	121-1-87.	13.205	0.171	0.0034	0.0025	0	0.0016	0.006	0	0.0006	0.1086	0.0007	0.0013	0.0008	0.0073	0.0098	0	0	0	0	0	0.0268
234	123-2-87.	13.142	0.181	0.0035	0.0023	0	0.0016	0.1786	0.0002	0.0007	0.1049	0.0008	0.0002	0.0007	0.0073	0.0102	0	0	0	0	0	0.029
235	125-3-87.	13.003	0.184	0.0036	0.002	0.0001	0.0017	0.4627	0.0005	0.0007	0.1018	0.0009	0.0001	0.0005	0.0072	0.0104	0	0	0	0	0	0.0217
236	131-4-87.	13.222	0.181	0.0038	0.0882	0	0.0017	0.4483	0.0005	0.0008	0.102	0.0008	0.0003	0.0004	0.0073	0.0104	0	0	0	0	0	0.0227
237	128-1-88.	13.145	0.612	0.0045	0.099	0	0.002	0.0076	0	0.0009	0.11	0.0008	0.0013	0.0007	0.0073	0.0105	0	0	0	0	0	0.0234
238	130-2-88.	13.192	0.616	0.0041	0.1019	0	0.002	0.2055	0.0003	0.0009	0.1068	0.0009	0.001	0.0007	0.0073	0.0106	0	0	0	0	0	0.0247

	SAMPLE	Silicon	Iron	Copper	Magnesium	Zinc	Nickel	Manganese	Lead	Chromium	Titanium	Tin	Calcium	Sodium	Vanadium	Gallium	Boron	Lithium	Berillium	Bismuth	Zirconium	Strontium
	#	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
239	122-1-89.	13.034	0.676	0.0038	0.0025	0.0011	0.0018	0.0081	0.0001	0.0009	0.1054	0.0011	0.0002	0.0006	0.0075	0.0104	0	0	0	0.0001	0	0.0214
240	124-2-89.	13.241	0.667	0.004	0.0019	0.0012	0.0021	0.2113	0.0004	0.001	0.1053	0.0011	0.0002	0.0009	0.0076	0.0106	0	0	0	0	0	0.0311
241	126-3-89.	12.945	0.675	0.004	0.0016	0.0017	0.0019	0.4629	0.0007	0.001	0.1003	0.0013	0.0001	0.0006	0.0075	0.0106	0	0	0	0.0002	0	0.0287
242	132-4-89.	13.017	0.654	0.0041	0.0922	0.0013	0.002	0.4557	0.0007	0.001	0.099	0.0012	0.0002	0.0005	0.0074	0.0106	0	0	0	0	0	0.0305
243	127-1-90.	13.238	0.182	0.0037	0.0979	0	0.0017	0.0092	0	0.0006	0.1078	0.0008	0.0003	0.0008	0.0074	0.0103	0	0	0	0	0	0.028
244	129-2-90.	13.07	0.188	0.0038	0.1189	0	0.0016	0.1768	0.0003	0.0007	0.1039	0.001	0.0002	0.0005	0.0073	0.0104	0	0	0	0.0001	0	0.0286
245	133-1-91.	13.029	0.18	0.0037	0.0017	0	0.0016	0.0061	0.0001	0.0007	0.1979	0.001	0.0001	0.0002	0.0074	0.0114	0	0	0	0	0	0.0232
246	137-2-91.	13.26	0.184	0.0038	0.0009	0	0.0017	0.4981	0.0008	0.0007	0.1993	0.0011	0.0001	0.0003	0.0075	0.0116	0	0	0	0	0	0.0273
247	139-1-92.	13.4	0.179	0.0039	0.1021	0	0.0018	0.0088	0.0002	0.0007	0.206	0.0009	0.0002	0.0007	0.0076	0.0118	0	0	0	0	0	0.0274
248	141-2-92.	13.422	0.18	0.004	0.0892	0	0.0018	0.2283	0.0005	0.0008	0.2013	0.0009	0.0001	0.0004	0.0076	0.0119	0	0	0	0	0	0.0281
249	140-1-93.	13.193	0.642	0.004	0.109	0	0.002	0.0077	0.0002	0.0009	0.2072	0.001	0.0002	0.0008	0.0076	0.012	0	0	0	0	0	0.0274
250	142-2-93.	13.181	0.633	0.0042	0.1461	0.0002	0.002	0.2006	0.0005	0.0009	0.2011	0.0011	0.0004	0.0007	0.0076	0.0122	0	0	0	0	0	0.0377
251	131-1-94.	12.841	0.714	0.0038	0.0035	0.0007	0.002	0.008	0	0.0001	0.0373	0.001	0.0002	0.0006	0.0074	0.0096	0	0	0	0	0	0.0288
252	136-2-94.	13.121	0.706	0.0041	0.0028	0.0012	0.0019	0.2049	0.0005	0.0011	0.2431	0.0012	0.0002	0.0007	0.0076	0.0125	0	0	0	0.0002	0.0001	0.0288
253	138-3-94.	13.245	0.689	0.0042	0.0024	0.0013	0.0021	0.4848	0.001	0.0011	0.2393	0.0013	0.0001	0.0006	0.0076	0.0125	0	0	0	0	0.0001	0.0282
254	144-4-94.	13.199	0.672	0.0043	0.1158	0.0009	0.0021	0.4732	0.001	0.0011	0.2333	0.0012	0.0001	0.0004	0.0076	0.0125	0	0	0	0	0.0001	0.032
255	169-1-95.	11.801	0.169	0.003	0.0019	0	0.0017	0.003	0	0.0004	0.0108	0.0007	0.0025	0.0017	0.0071	0.0094	0	0	0	0	0	0.0002
256	170-2-95.	11.746	0.17	0.0033	0.0015	0	0.0017	0.0037	0	0.0004	0.0103	0.0007	0	0.003	0.0069	0.0095	0	0	0	0	0	0.0002
257	171-1-96.	11.464	0.162	0.0024	0.0011	0	0.0016	0.0028	0	0.0003	0.0092	0.0006	0	0.009	0.006	0.0091	0	0	0	0	0	0.0003
258	172-2-96.	11.615	0.167	0.0027	0.0015	0	0.0018	0.0038	0	0.0004	0.0093	0.0008	0	0.0098	0.0062	0.0092	0	0	0	0	0	0.0003
259	200-1-97.	11.574	0.163	0.0026	0.001	0	0.0017	0.0028	0	0.0003	0.1051	0.0007	0	0.005	0.0064	0.0105	0	0	0	0	0	0.0002
260	201-2-97.	11.781	0.157	0.0028	0.0003	0	0.0016	0.0034	0	0.0003	0.0994	0.0005	0.0001	0.0336	0.0066	0.011	0	0	0	0	0	0.0006
261	199-1-98.	11.298	0.162	0.0025	0.0011	0	0.0017	0.0028	0	0.0003	0.1108	0.0008	0	0.0007	0.0062	0.0104	0	0	0	0	0	0
262	203-2-98.	11.535	0.163	0.0026	0.001	0	0.0017	0.0036	0	0.0004	0.1087	0.0007	0	0.0006	0.0062	0.0104	0	0	0	0	0	0.0358
263	177-1-99.	11.732	0.167	0.0029	0.0015	0	0.0017	0.0029	0	0.0004	0.0102	0.0007	0	0.0009	0.0071	0.0094	0	0	0	0	0	0.0048
264	178-2-99.	11.901	0.168	0.0031	0.0017	0	0.0017	0.0037	0	0.0005	0.0102	0.0008	0	0.0007	0.0071	0.0093	0	0	0	0	0	0.0093
265	179-1-100	11.705	0.163	0.0029	0.0015	0	0.0017	0.0028	0	0.0004	0.0099	0.0007	0	0.0006	0.0066	0.0092	0	0	0	0	0	0.0195
266	181-2-100	11.985	0.164	0.0029	0.0012	0	0.0017	0.0035	0	0.0004	0.0099	0.0007	0	0.0006	0.0067	0.0092	0	0	0	0	0	0.0284
267	197-1-101	11.959	0.62	0.0035	0.105	0	0.002	0.4918	0.0006	0.0006	0.1944	0.0011	0.0004	0.0004	0.0072	0.0123	0	0	0	0	0	0.0289
268	198-2-101	11.702	0.616	0.0033	0.1228	0	0.002	0.4929	0.0007	0.0006	0.1914	0.0011	0.0002	0.0003	0.007	0.0122	0	0	0	0	0	0.0262
269	185-1-102	11.556	0.614	0.0034	0.1043	0	0.002	0.5125	0.0006	0.0005	0.1717	0.001	0	0.0137	0.0066	0.0122	0	0	0	0	0	0.0001
270	186-2-102	11.625	0.624	0.0031	0.118	0	0.0019	0.519	0.0007	0.0006	0.1698	0.001	0.0001	0.0125	0.0069	0.0122	0	0	0	0	0	0.0001
271	14-1-103.	10.605	0.6	0.0032	0.002	0	0.002	0.0058	0	0.0005	0.1046	0.0008	0.0031	0.0122	0.0061	0.0109	0	0	0	0	0	0
272	18-2-103.	10.33	0.616	0.0027	0.0011	0	0.002	0.48	0.0008	0.0005	0.0997	0.0011	0.0001	0.0089	0.006	0.0113	0	0	0	0	0	0
273	16-1-104.	10.393	0.62	0.0026	0.0009	0	0.002	0.2001	0.0003	0.0005	0.1005	0.0009	0.0002	0.02	0.0061	0.0113	0	0	0	0	0	0.0001
274	22-2-104.	10.586	0.609	0.0031	0.1004	0	0.002	0.1947	0.0002	0.0005	0.1007	0.0008	0.0029	0.0146	0.006	0.0113	0	0	0	0	0	0.0001
275	57-1-105.	10.434	0.151	0.0027	0.1049	0	0.0017	0.1999	0.0001	0.0003	0.0674	0.0008	0	0.0006	0.0063	0.0107	0	0	0	0	0	0.0268
276	58-2-105.	10.554	0.586	0.0033	0.1123	0	0.002	0.1959	0.0003	0.0006	0.1321	0.001	0.0002	0.0008	0.0063	0.0117	0	0	0	0	0	0.0282
277	52-1-106.	10.367	0.622	0.0028	0.0021	0	0.002	0.1924	0.0002	0.0005	0.1096	0.001	0	0.0007	0.0063	0.0111	0	0	0	0	0	0.0251
278	70-2-106.	10.364	0.597	0.0028	0.1091	0	0.002	0.1869	0.0004	0.0005	0.1981	0.0011	0.0001	0.0006	0.0063	0.0125	0	0	0	0	0	0.0253
279	25-1-107.	10.711	0.15	0.0028	0.0018	0	0.0018	0.0037	0	0.0003	0.1913	0.0009	0.0002	0.0143	0.0063	0.0125	0	0	0	0	0	0.0002
280	31-2-107.	10.665	0.146	0.0029	0.1119	0	0.0018	0.0042	0	0.0003	0.1933	0.0009	0	0.0172	0.0063	0.0126	0	0	0	0	0	0
281	50-1-108.	10.559	0.564	0.0029	0.0029	0	0.0021	0.0065	0	0.0005	0.1039	0.0011	0.0001	0.0009	0.0064	0.0111	0	0	0	0	0	0.0255
282	58-2-108.	10.676	0.56	0.003	0.1113	0	0.0018	0.2002	0.0003	0.0005	0.1033	0.0012	0.0001	0.0006	0.0065	0.0113	0	0	0	0	0	0.0264
283	57-1-109.	10.782	0.152	0.0021	0.1086	0	0.0018	0.2051	0.0002	0.0004	0.1031	0.001	0.0004	0.0012	0.0064	0.0112	0	0	0	0	0	0.0271
284	71-2-109.	10.805	0.152	0.003	0.12	0	0.0018	0.5048	0.0007	0.0004	0.2084	0.0012	0.0003	0.0009	0.0064	0.0128	0	0	0	0	0	0.0336
285	91-1-110.	13.385	0.173	0.0038	0.1007	0	0.0017	0.0058	0	0.0006	0.1056	0.0008	0.0002	0.0101	0.0075	0.0106	0	0	0	0	0	0.0002
286	93-2-110.	13.474	0.176	0.004	0.1028	0	0.0017	0.1075	0	0.0007	0.103	0.0008	0.0002	0.0145	0.0076	0.0107	0	0	0	0	0	0.0002
287	173-1-111	11.962	0.164	0.003	0.001	0	0.0018	0.0027	0	0.0003	0.01	0.0008	0.0001	0.0106	0.007	0.0096	0	0	0	0	0	0.0005

	SAMPLE	Silicon	Iron	Copper	Magnesium	Zinc	Nickel	Manganese	Lead	Chromium	Titanium	Tin	Calcium	Sodium	Vanadium	Gallium	Boron	Lithium	Berillium	Bismuth	Zirconium	Strontium
	#	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
288	174-2-111	11.982	0.164	0.0032	0.0003	0	0.0018	0.0033	0	0.0004	0.0099	0.0008	0	0.0174	0.007	0.0097	0	0	0	0	0	0.0003
289	182-1-112	11.933	0.167	0.003	0.001	0	0.0018	0.0029	0	0.0004	0.0101	0.0009	0.0001	0.0005	0.007	0.0093	0	0	0	0	0	0.0279
290	183-2-112	12.191	0.166	0.0031	0.0009	0	0.0018	0.0036	0	0.0004	0.0103	0.0009	0.0001	0.0004	0.007	0.0094	0	0	0	0	0	0.0352
291	185-1-113	11.898	0.567	0.0033	0.1061	0	0.0022	0.5087	0	0.0006	0.1926	0.0013	0.0004	0.0041	0.0073	0.0125	0	0	0	0	0	0.0002
292	186-2-113	11.929	0.547	0.0036	0.1143	0	0.0021	0.4944	0.0006	0.0006	0.1863	0.0012	0.0003	0.0122	0.0072	0.0126	0	0	0	0	0	0.0004
293	175-1-114	11.743	0.161	0.003	0.0007	0	0.0016	0.0027	0	0.0003	0.0098	0.0006	0.0009	0.0386	0.007	0.0099	0	0	0	0	0	0.0001
294	176-2-114	11.665	0.158	0.0032	0	0	0.0017	0.0033	0	0.0004	0.0094	0.0005	0	0.0534	0.007	0.0102	0	0	0	0	0	0.0002
295	180-1-115	11.664	0.173	0.0028	0.0027	0	0.0017	0.0068	0.0005	0.0004	0.012	0.0008	0	0.0001	0.0068	0.0093	0	0	0	0	0	0.0305
296	182-2-115	11.49	0.174	0.0029	0.0029	0	0.0017	0.008	0.0005	0.0005	0.0118	0.0008	0.0002	0.0002	0.0067	0.0093	0	0	0	0	0	0.0683
297	189-1-116	11.682	0.593	0.0033	0.1008	0	0.002	0.5178	0.0008	0.0007	0.1893	0.0011	0.0002	0.0416	0.0073	0.0132	0	0	0	0	0	0.0002
298	190-2-116	11.515	0.553	0.0036	0.1023	0	0.002	0.4932	0.0008	0.0007	0.1785	0.001	0.0001	0.0668	0.0075	0.0136	0	0	0	0	0	0.0003
299	192-1-117	11.31	0.584	0.0031	0.1072	0	0.002	0.5145	0.0015	0.0006	0.1951	0.0013	0	0.0001	0.007	0.0124	0	0	0	0	0	0.0053
300	193-2-117	11.59	0.578	0.0032	0.1475	0	0.002	0.5112	0.0016	0.0006	0.1958	0.0013	0.0001	0	0.007	0.0124	0	0	0	0	0	0.0132
301	194-1-118	11.555	0.66	0.0032	0.1075	0	0.0021	0.5351	0.0016	0.0008	0.1998	0.0013	0	0.0002	0.0071	0.0125	0	0	0	0	0	0.0212
302	195-2-118	11.605	0.641	0.0032	0.1496	0	0.0021	0.5235	0.0016	0.0007	0.1973	0.0013	0.0002	0.0002	0.007	0.0124	0	0	0	0	0	0.0424
303	197-1-119	11.64	0.731	0.0032	0.1087	0	0.0021	0.5	0.0019	0.0008	0.1995	0.0013	0.0001	0.0003	0.0071	0.0125	0	0	0	0	0	0.046
304	198-2-119	11.196	0.71	0.0032	0.1494	0	0.002	0.4877	0.0019	0.0007	0.1908	0.0013	0.0002	0.0001	0.0069	0.0124	0	0	0	0	0	0.0951
305	154-1-120	11.514	0.535	0.0031	0.001	0	0.0019	0.1722	0.0005	0.0005	0.1913	0.0011	0	0.0211	0.0069	0.0124	0	0	0	0	0	0
306	191-2-120	11.625	0.481	0.0034	0.1103	0	0.0019	0.4238	0.0009	0.0005	0.1753	0.001	0	0.0567	0.0074	0.0134	0	0	0	0.0006	0	0.0001
307	92-1-121.	12.461	0.658	0.0037	0.0991	0	0.0019	0.0097	0	0.0008	0.0985	0.0008	0.0001	0.0222	0.0072	0.0109	0	0	0	0.0003	0	0.0002
308	108-2-121	12.814	0.669	0.0041	0.1058	0	0.0021	0.5194	0.0008	0.001	0.2056	0.0012	0	0.0132	0.0075	0.0124	0	0	0	0	0	0.0001
309	103-1-122	12.404	0.171	0.0032	0.1009	0	0.0016	0.0056	0	0.0003	0.2061	0.0008	0	0.0133	0.0073	0.012	0	0	0	0	0	0
310	107-2-122	12.483	0.178	0.0034	0.1072	0	0.0016	0.5965	0.0007	0.0005	0.1967	0.001	0	0.0136	0.0074	0.0122	0	0	0	0	0	0.0001
311	173-1-123	11.863	0.164	0.003	0.0013	0	0.0016	0.0044	0	0.0003	0.0105	0.0007	0	0.0272	0.007	0.0098	0	0	0	0	0	0
312	174-2-123	11.719	0.161	0.0031	0.0008	0	0.0016	0.0052	0	0.0003	0.0103	0.0006	0	0.0379	0.0069	0.0099	0	0	0	0	0	0
313	41-1-124.	10.668	0.162	0.003	0.0023	0	0.0018	0.5396	0.0008	0.0006	0.0085	0.001	0.0004	0.0003	0.0061	0.0097	0	0	0	0	0	0.0303
314	60-2-124.	10.452	0.622	0.0032	0.1072	0	0.002	0.5144	0.0009	0.0008	0.1066	0.0012	0.0003	0.0002	0.0061	0.0112	0	0	0	0	0	0.0459
315	195-1-125	11.56	0.713	0.0033	0.1097	0	0.0022	0.5821	0.0009	0.0007	0.2023	0.0013	0.0002	0.0008	0.0071	0.0126	0	0	0	0	0	0.0274
316	198-2-125	11.601	0.703	0.0034	0.1284	0	0.0022	0.5734	0.0009	0.0008	0.1982	0.0013	0.0002	0.0007	0.0071	0.0126	0	0	0	0	0	0.0504
317	184-1-126	11.27	0.632	0.0032	0.1095	0	0.0022	0.5361	0.0008	0.0006	0.2057	0.0012	0	0.0005	0.007	0.0125	0	0	0	0	0	0.0001
318	189-2-126	11.71	0.589	0.0035	0.1163	0	0.0021	0.5156	0.0007	0.0007	0.1887	0.001	0.0002	0.034	0.0073	0.0132	0	0	0	0	0	0.0005
319	182-1-127	11.815	0.165	0.0029	0.0006	0	0.0018	0.0028	0	0.0004	0.0103	0.0007	0.0001	0.0003	0.0069	0.0093	0	0	0	0	0	0.0366
320	183-2-127	11.721	0.167	0.0029	0.0005	0	0.0018	0.0036	0	0.0005	0.0101	0.0008	0.0003	0.0003	0.0098	0.0092	0	0	0	0	0	0.0476
321	180-1-128	11.768	0.166	0.0029	0.0007	0	0.0018	0.0028	0	0.0004	0.0102	0.0007	0	0.0003	0.0069	0.0093	0	0	0	0	0	0.024
322	164-2-128	11.732	0.64	0.0032	0.1102	0	0.0021	0.1767	0.0002	0.0007	0.1241	0.001	0	0.0002	0.007	0.0112	0	0	0	0	0	0.0258
323	173-1-129	11.718	0.168	0.0029	0.0007	0	0.0017	0.0041	0	0.0005	0.011	0.0006	0	0.0115	0.0069	0.0096	0	0	0	0	0	0.0004
324	146-2-129	11.565	0.608	0.0032	0	0	0.0021	0.2036	0.0001	0.0007	0.0106	0.0008	0	0.0113	0.0069	0.0097	0	0	0	0	0	0.0001
325	41-1-130.	10.393	0.156	0.0026	0.0004	0	0.0018	0.2314	0.0002	0.0004	0.0091	0.0008	0	0.0007	0.0062	0.0096	0	0	0	0	0	0.0242
326	60-2-130.	10.346	0.696	0.0029	0.1145	0	0.0022	0.2216	0.0004	0.0006	0.1238	0.0011	0	0.0004	0.0062	0.0116	0	0	0	0	0	0.0262
327	81-1-131.	13.187	0.179	0.0037	0.1022	0	0.0017	0.1826	0	0.0006	0.0119	0.0006	0	0.0155	0.0074	0.0097	0	0	0	0	0	0.0004
328	288-2-131	12.858	0.631	0.004	0.0964	0	0.0021	0.515	0.0006	0.0009	0.1311	0.001	0.0001	0.0098	0.0096	0.0113	0.017	0	0	0	0	0.0001
329	120-1-132	12.943	0.765	0.004	0.1031	0	0.0022	0.5973	0.0007	0.001	0.0111	0.0011	0.0002	0.0005	0.0075	0.0097	0	0	0	0	0	0.0255
330	289-2-132	12.77	0.734	0.0041	0.1132	0	0.0022	0.5693	0.0008	0.001	0.111	0.0011	0.0001	0.0005	0.009	0.0109	0.0113	0	0	0	0	0.0298
331	173-1-133	11.701	0.171	0.0029	0.0019	0	0.0016	0.0076	0.0007	0.0004	0.0108	0.0007	0	0.0071	0.0069	0.0094	0	0	0	0	0	0
332	153-2-133	11.763	0.168	0.0032	0.0006	0	0.0017	0.214	0.0014	0.0005	0.2207	0.0008	0	0.0127	0.007	0.0126	0	0	0	0	0	0
333	41-1-134.	10.337	0.157	0.0031	0.0017	0	0.0018	0.555	0.0013	0.0004	0.0085	0.0009	0	0.0001	0.0062	0.0098	0	0	0	0	0	0.0305
334	60-2-134.	10.262	0.691	0.003	0.1168	0	0.0022	0.5255	0.0016	0.0008	0.1008	0.0011	0.0001	0.0001	0.0063	0.0114	0	0	0	0	0	0.0436
335	173-1-135	11.618	0.162	0.0027	0.0013	0	0.0017	0.0045	0.0005	0.0003	0.0111	0.0006	0	0.0177	0.0067	0.0093	0	0	0	0	0	0
336	212-2-135	11.337	0.164	0.0029	0.0004	0	0.0018	0.0054	0.0008	0.0005	0.01368	0.0007	0.0001	0.0118	0.0087	0.0112	0.0191	0	0	0	0	0

	SAMPLE	Silicon	Iron	Copper	Magnesium	Zinc	Nickel	Manganese	Lead	Chromium	Titanium	Tin	Calcium	Sodium	Vanadium	Gallium	Boron	Lithium	Berillium	Bismuth	Zirconium	Strontium
	#	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
337	224-1-136	12.039	0.168	0.0017	0.0022	0	0.0017	0.0032	0.0003	0.0003	0.0999	0.0007	0.0001	0.0002	0.0064	0.0092	0.011	0	0	0	0	0
338	227-2-136	12.301	0.173	0.0019	0.0018	0	0.0016	0.004	0.0004	0.0004	0.0891	0.0006	0.0001	0.0057	0.0062	0.0093	0.0079	0	0	0	0	0.0001
338	252-1-137	12.499	0.175	0.0032	0.0686	0	0.0017	0.0029	0.0001	0.0004	0.0957	0.0007	0	0.0001	0.0089	0.0105	0.0088	0	0	0	0	0.0184
340	289-2-137	12.433	0.463	0.0034	0.1661	0	0.0019	0.4618	0.0009	0.0007	0.0893	0.001	0.0003	0.0001	0.009	0.0109	0.008	0	0	0	0	0.0639
341	261-1-138	12.318	0.645	0.0033	0.0038	0	0.0021	0.0085	0.0003	0.0007	0.0861	0.0009	0	0.0001	0.0087	0.0105	0.0059	0	0	0	0	0.0303
342	264-2-138	12.311	0.66	0.0035	0.0042	0.0002	0.0021	0.5583	0.0011	0.0009	0.0847	0.0011	0.0003	0.0003	0.0089	0.0109	0.0064	0	0	0	0	0.0577
343	218-1-139	12.435	0.292	0.0018	0.0017	0	0.0033	0.0103	0.0007	0.0005	0.0936	0.0007	0.0003	0.0131	0.0101	0.0115	0.0094	0	0	0	0	0.0007
344	233-2-139	12.321	0.29	0.0019	0.0006	0	0.0032	0.0103	0.001	0.0006	0.0866	0.0007	0	0.0212	0.0099	0.0116	0.0071	0	0	0	0	0
345	238-1-140	12.131	0.291	0.0012	0.0014	0	0.0033	0.0035	0.0007	0.0003	0.0976	0.0008	0	0.0003	0.0103	0.0116	0.0103	0	0	0	0	0.0314
346	240-2-140	12.046	0.293	0.0013	0.0015	0	0.0033	0.0013	0.001	0.0004	0.0887	0.0008	0.0003	0.0003	0.0099	0.0114	0.0075	0	0	0	0.0001	0.0637
347	255-1-141	12.35	0.273	0.0014	0.0015	0	0.0032	0.192	0.0004	0.0003	0.0906	0.0009	0	0.0001	0.0099	0.0108	0.0083	0	0	0	0	0.0261
348	258-2-141	12.244	0.285	0.0016	0.0018	0	0.0032	0.5161	0.0011	0.0004	0.0856	0.001	0.0003	0.0001	0.0099	0.0112	0.0072	0	0	0	0	0.0658
349	274-1-142	12.426	0.29	0.0014	0.0015	0	0.0034	0.0086	0.0005	0.0003	0.1979	0.0009	0.0004	0.0002	0.0093	0.0126	0.0023	0	0	0	0	0.0304
350	278-2-142	12.724	0.753	0.0018	0.1221	0.0003	0.0037	0.5125	0.0014	0.0008	0.179	0.0013	0.0005	0.0008	0.0101	0.0134	0.0007	0	0	0	0.0001	0.0619
351	275-1-143	12.39	0.289	0.0014	0.0018	0	0.0034	0.0076	0.0002	0.0003	0.1634	0.0009	0.0001	0.0002	0.0099	0.0121	0.0056	0	0	0	0	0.0269
352	279-2-143	12.264	0.594	0.0017	0.1101	0	0.0036	0.487	0.001	0.0006	0.1948	0.0012	0.0003	0.0002	0.0109	0.013	0.0146	0	0	0	0.0001	0.0547
353	276-1-144	12.529	0.26	0.0016	0.0029	0	0.0032	0.0067	0.0002	0.0003	0.1501	0.0008	0	0.0001	0.01	0.0117	0.0072	0	0	0	0	0.0248
354	280-2-144	12.154	0.646	0.0019	0.113	0	0.0034	0.4749	0.0011	0.0006	0.1948	0.0012	0.0003	0.0001	0.0115	0.0128	0.0254	0	0	0	0.0001	0.0626
355	236-1-146	12.222	0.294	0.0012	0.0014	0	0.0035	0.0037	0.0002	0.0003	0.0849	0.0008	0	0.0001	0.0099	0.011	0.006	0	0	0	0	0.0088
356	264-2-146	12.097	0.709	0.0016	0.1083	0.0008	0.0037	0.5027	0.0012	0.0006	0.0866	0.0011	0.0003	0	0.0102	0.0118	0.008	0	0	0	0.0001	0.0409
357	28-1-148.	10.015	0.663	0.0015	0.0006	0	0.0033	0.1498	0.0005	0.0004	0.1796	0.0011	0	0.0084	0.0073	0.0129	0.0001	0	0	0	0	0
358	60-1-149.	9.8951	0.681	0.0017	0.1103	0	0.0033	0.5208	0.0011	0.0005	0.1012	0.0013	0	0.0003	0.0073	0.0123	0	0	0	0	0	0.02
359	32-1-150.	10.096	0.575	0.0017	0.1099	0	0.0031	0.0066	0.0008	0.0004	0.209	0.0011	0	0.0158	0.0072	0.0135	0	0	0	0	0	0
360	134-1-151	12.501	0.664	0.0019	0.0025	0	0.0035	0.0125	0.0005	0.0007	0.2038	0.001	0.0001	0.0001	0.0082	0.0123	0	0	0	0	0.0001	0.0326
361	215-1-152	11.8	0.281	0.003	0.0012	0	0.0033	0.0034	0.0002	0.0002	0.0945	0.0009	0	0	0.0098	0.0113	0.0081	0	0	0	0	0.0246
362	221-2-152	11.842	0.281	0.0024	0.0014	0	0.0034	0.0043	0.0005	0.0003	0.0964	0.001	0.0002	0.0001	0.0098	0.0114	0.0089	0	0	0	0	0.0467
363	230-1-153	12.316	0.287	0.0014	0.0014	0	0.0034	0.0034	0.0005	0.0003	0.096	0.0009	0	0.0098	0.0102	0.0116	0.0085	0	0	0	0	0
364	233-2-153	12.387	0.282	0.0016	0	0	0.0033	0.0042	0.0013	0.0005	0.0815	0.0008	0	0.0245	0.0099	0.0116	0.0046	0	0	0	0	0
365	206-1-154	10.091	0.208	0.0048	0.0012	0	0.0027	0.0038	0.0004	0.0002	0.1153	0.0008	0	0.0072	0.0074	0.0109	0.0168	0	0	0	0	0
366	258-2-154	12.281	0.283	0.0014	0.0015	0	0.0032	0.5666	0.0021	0.0005	0.0858	0.0012	0.0003	0.0002	0.0093	0.0111	0.006	0	0	0	0	0.0639
367	240-1-154	12.279	0.274	0.0012	0.0013	0	0.0032	0.0034	0.0007	0.0003	0.0832	0.001	0	0.0001	0.0091	0.0107	0.0041	0	0	0	0	0.0423
368	209-1-155	10.195	0.228	0.0032	0.001	0	0.0029	0.0032	0.0007	0.0004	0.1073	0.0009	0	0	0.0087	0.0115	0.0131	0	0	0	0	0.0249
369	274-1-155	12.484	0.282	0.0014	0.0014	0	0.0033	0.0079	0.0004	0.0003	0.2015	0.001	0	0	0.0097	0.0126	0.0058	0	0	0	0	0.0273
370	278-2-155	12.48	0.631	0.0017	0.1209	0	0.0036	0.4001	0.0014	0.0005	0.1832	0.0012	0.0002	0.0001	0.0097	0.0129	0.0029	0	0	0	0.0001	0.0429
371	275-1-156	12.083	0.266	0.0013	0.0022	0	0.0031	0.008	0.0004	0.0002	0.1282	0.001	0	0	0.0093	0.0111	0.0049	0	0	0	0	0.0268
372	221-1-156	12.672	0.267	0.0036	0.0029	0	0.003	0.0081	0.0007	0.0006	0.1167	0.0009	0.0013	0.0003	0.0093	0.0108	0.0144	0	0	0	0.0001	0.0261
373	279-2-156	12.019	0.645	0.0016	0.1184	0	0.0034	0.5275	0.0016	0.0006	0.2481	0.0014	0.0003	0.0001	0.0131	0.0131	0.0462	0	0	0	0.0001	0.0641
374	233-1-157	12.379	0.26	0.0021	0.0011	0	0.0031	0.0125	0.0002	0.0004	0.1062	0.0007	0	0.0249	0.0098	0.0114	0.0123	0	0	0	0	0
375	258-1-158	12.179	0.279	0.0031	0.0012	0	0.0033	0.4725	0.0015	0.0003	0.118	0.001	0	0.0001	0.0108	0.0118	0.0163	0	0	0	0	0
376	264-1-159	12.116	0.763	0.0044	0.1069	0.0007	0.0035	0.4935	0.0019	0.0006	0.0983	0.0012	0	0.0001	0.0098	0.0113	0.0123	0	0	0	0	0.0239
377	275-1-160	12.236	0.26	0.002	0.0033	0	0.003	0.013	0.0005	0.0005	0.1342	0.0009	0.0004	0.0005	0.0089	0.0108	0.0046	0	0	0	0	0.0156
378	279-1-161	12.179	0.724	0.0033	0.1076	0	0.0035	0.5172	0.0014	0.0008	0.2114	0.0012	0.0003	0.0001	0.00126	0.0128	0.0358	0	0	0	0.0001	0.0255
379	292-1-162	12.193	0.752	0.0038	0.1058	0	0.0035	0.0123	0.0009	0.0005	0.0804	0.0011	0.0001	0.0002	0.0092	0.0109	0.0053	0	0	0	0.0001	0.0228
380	189-1-163	12.821	0.382	0.0025	0.1097	0	0.003	0.5485	0.0011	0.0008	0.078	0.0011	0.0007	0	0.0093	0.0109	0.0051	0	0	0	0.0001	0.0256
381	293-1-164	12.169	0.264	0.0015	0.1045	0	0.003	0.5181	0.0011	0.0003	0.0706	0.001	0	0	0.0083	0.0107	0.0034	0	0	0	0	0.0231
382	278-1-165	12.117	0.733	0.0018	0.0969	0	0.0035	0.4943	0.0012	0.0005	0.1958	0.0012	0	0.0001	0.0095	0.0128	0.0089	0	0	0	0.0001	0.0228
383	291-1-166	12.061	0.733	0.0142	0.0017	0	0.0033	0.5252	0.0017	0.0007	0.0741	0.0012	0.0002	0.0005	0.0008	0.0104	0.0041	0	0	0	0	0.0254
384	283-1-167	11.954	0.243	0.0054	0.0015	0	0.0028	0.0049	0.0003	0	0.0048	0.0008	0.0001	0.0005	0.0004	0.0092	0.0232	0	0	0	0	0.0081
385	169-1-168	12.008	0.27	0.0029	0.0016	0	0.0031	0.0082	0.0005	0.0003	0.0095	0.0008	0	0.0001	0.0077	0.0095	0	0	0	0	0	0

	SAMPLE	Silicon	Iron	Copper	Magnesium	Zinc	Nickel	Manganese	Lead	Chromium	Titanium	Tin	Calcium	Sodium	Vanadium	Gallium	Boron	Lithium	Berillium	Bismuth	Zirconium	Strontium
	#	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
386	233-1-169	12.313	0.23	0.0143	0.0011	0	0.0027	0.0031	0.001	0.0004	0.1521	0.0008	0	0.0167	0.0102	0.0113	0.0259	0	0	0	0	0
387	258-1-170	12.186	0.273	0.0014	0.002	0	0.0031	0.4595	0.0011	0.0003	0.0809	0.001	0	0.0001	0.0086	0.0107	0.0036	0	0	0	0	0.0152
388	277-1-171	11.988	0.291	0.0033	0.0017	0	0.0036	0.0048	0.0012	0	0.0435	0.0008	0.0001	0.0002	0.0022	0.0104	0.0038	0	0	0	0	0.016
389	269-1-172	12.171	0.284	0.0017	0.0016	0	0.0033	0.0035	0.0008	0.0002	0.0079	0.0008	0.0001	0.0001	0.0042	0.0097	0.0051	0	0	0	0	0.0214
390	269-1-173	11.618	0.296	0.003	0.0016	0	0.0036	0.0046	0.001	0.0001	0.001	0.0008	0.0001	0.0001	0.0011	0.0102	0.037	0	0	0	0	0.0137
391	282-1-174	12.195	0.29	0.0029	0.0016	0	0.0036	0.0049	0.0015	0.0002	0.0792	0.0008	0.0002	0.0002	0.0056	0.0108	0.0045	0	0	0	0	0.0188
392	205-1-175	10.208	0.247	0.0026	0.0009	0	0.0034	0.0042	0.0008	0	0.0009	0.0007	0	0.0195	0.0004	0.0104	0.0354	0	0	0	0	0.0001
393	278-1-176	12.225	0.68	0.0027	0.1002	0	0.0039	0.5002	0.0021	0.0007	0.242	0.0012	0	0.0002	0.0096	0.0135	0.0044	0	0	0	0.0001	0.0219
394	169-1-177	10.972	0.275	0.0022	0.0014	0	0.0036	0.0095	0.0004	0.0002	0.0108	0.0007	0.0001	0.0001	0.0085	0.0104	0	0	0	0	0	0
395	207-1-178	9.876	0.235	0.0152	0.0013	0	0.0031	0.0031	0.0013	0.0002	0.0734	0.0009	0	0.009	0.0042	0.011	0.0063	0	0	0	0	0
396	208-1-179	9.9325	0.237	0.0015	0.0015	0	0.003	0.0035	0.0004	0.0003	0.0001	0.0009	0.0003	0.0001	0.0004	0.01	0.0416	0	0	0	0	0.0167
397	211-1-180	11.573	0.287	0.0023	0.0012	0	0.0034	0.0035	0.0014	0.0003	0.0457	0.0008	0	0.0095	0.0022	0.01	0.0051	0	0	0	0	0
398	214-1-181	11.715	0.263	0.0014	0.002	0	0.0031	0.0035	0.0002	0.0002	0.0339	0.0008	0	0.0001	0.0018	0.0101	0.0024	0	0	0	0	0.0182
399	217-1-182	12.484	0.253	0.0027	0.002	0	0.0028	0.0097	0.0014	0.0006	0.0009	0.0007	0.0002	0.0095	0.0005	0.0092	0.0318	0	0	0	0	0.0002
400	220-1-183	12.432	0.257	0.0025	0.0033	0.0002	0.0029	0.0102	0.0005	0.0007	0.0007	0.0008	0.0003	0	0.0008	0.0092	0.0404	0	0	0	0	0.0154
401	225-1-184	11.494	0.258	0.0016	0.0023	0	0.0031	0.0044	0.0001	0.0004	0.0435	0.0008	0.0004	0.0003	0.0025	0.0099	0.0026	0	0	0	0	0.0002
402	207-1-185	9.9704	0.222	0.0013	0.0009	0	0.0035	0.0035	0.0004	0.0011	0.351	0.001	0	0.0178	0.017	0.0144	0.1188	0	0	0	0.0001	0
403	211-1-186	11.436	0.278	0.0011	0.0007	0	0.0037	0.0036	0	0.0009	0.0146	0.0008	0	0.009	0.007	0.0104	0.0715	0	0	0	0	0
404	214-1-187	11.384	0.288	0.0012	0.0012	0	0.0038	0.0037	0.0001	0.0008	0.0031	0.0008	0	0.0001	0.003	0.0101	0.0457	0	0	0	0	0.0174
405	233-1-188	11.704	0.252	0.0013	0.0017	0	0.0031	0.0035	0.0002	0.0006	0.0048	0.0008	0	0.0001	0.0037	0.0095	0.0492	0	0	0	0	0.0003
406	226-1-189	11.953	0.25	0.0011	0.0011	0	0.0031	0.0036	0.0005	0.0005	0.0006	0.0008	0	0.0083	0.0008	0.0092	0.0442	0	0	0	0	0
407	229-1-190	11.954	0.291	0.0013	0.0006	0	0.0037	0.0036	0.0004	0.0007	0.001	0.0007	0	0.013	0.0012	0.0103	0.0392	0	0	0	0	0
408	232-1-191	11.945	0.256	0.0011	0.0005	0	0.0034	0.003	0.0002	0.0006	0.0045	0.0006	0	0.0354	0.0042	0.0105	0.0661	0	0	0	0	0
409	235-1-192	11.513	0.289	0.0479	0.0016	0	0.0037	0.0036	0.0002	0.0007	0.0101	0.0009	0.0001	0.0001	0.01	0.0103	0.0637	0	0	0	0.0001	0.0103
410	239-1-193	11.657	0.286	0.0117	0.0019	0	0.0036	0.0036	0.0002	0.0005	0.0065	0.0008	0.0001	0.0001	0.0061	0.0105	0.0569	0	0	0	0	0.0304
411	251-1-194	11.718	0.266	0.0081	0.1038	0	0.0037	0.0034	0.0001	0.0014	0.0208	0.0007	0.0003	0.0002	0.0217	0.0109	0.1438	0	0.0001	0	0.0005	0.0466
412	254-1-195	11.519	0.292	0.0011	0.0016	0	0.0036	0.2005	0.0016	0.0003	0.0036	0.0009	0	0.0001	0.0036	0.0104	0.042	0	0	0	0	0.0148
413	257-1-196	11.522	0.242	0.0015	0.0023	0	0.0029	0.5249	0.0016	0.0008	0.0147	0.001	0.0001	0.0001	0.0122	0.0099	0.0777	0	0	0	0.0002	0.0336
414	263-1-197	11.414	0.648	0.0012	0.0018	0	0.0035	0.5159	0.0019	0.0004	0.0038	0.0011	0	0.0001	0.0035	0.01	0.0514	0	0	0	0	0.0176
415	267-1-198	11.917	0.288	0.0012	0.0018	0	0.0035	0.0072	0.0007	0.0005	0.0108	0.0009	0	0.0001	0.0101	0.0103	0.0366	0	0	0	0.0001	0.0245
416	273-1-199	11.381	0.668	0.0013	0.0977	0	0.0038	0.5175	0.0016	0.0009	0.008	0.0012	0.0001	0.0001	0.0075	0.0106	0.0615	0	0	0	0	0.0226
417	260-1-200	11.636	0.342	0.0011	0.0021	0	0.0037	0.0112	0.0008	0.0006	0.0033	0.0009	0	0.0001	0.0032	0.0102	0.0469	0	0	0	0	0.0159
418	233-1-201	12.112	0.229	0.001	0.0012	0	0.0029	0.0043	0.0014	0.0013	0.1549	0.0007	0	0.0329	0.01	0.0111	0.0303	0	0	0	0	0.0001
419	213-1-202	11.808	0.282	0.0026	0.0015	0	0.004	0.0039	0.0008	0.0021	0.3498	0.0008	0	0.0149	0.0275	0.0146	0.104	0	0	0	0.0004	0
420	216-1-203	11.733	0.285	0.0033	0.0014	0	0.0037	0.0036	0.0006	0.0011	0.207	0.0009	0	0.0002	0.0165	0.0129	0.064	0	0	0	0.0002	0.0227
421	285-1-204	11.953	0.303	0.0026	0.0014	0	0.0037	0.0037	0.001	0.0011	0.0215	0.0008	0	0.0001	0.008	0.0105	0.0105	0	0	0	0	0.0235
422	270-1-205	11.833	0.77	0.0021	0.1077	0	0.0043	0.5575	0.0024	0.0018	0.0075	0.0011	0	0.0001	0.008	0.0111	0.0058	0	0	0	0	0.0177
423	271-1-206	11.815	0.81	0.0021	0.1053	0	0.0043	0.5319	0.0015	0.0016	0.0034	0.0011	0	0.0001	0.0034	0.0112	0.0189	0	0	0	0	0.022
424	207-1-207	9.6469	0.238	0.001	0.0013	0	0.0035	0.0041	0.0005	0.0016	0.4066	0.001	0	0.014	0.0285	0.0157	0.1254	0	0	0	0.0005	0
425	210-1-208	9.7673	0.238	0.0008	0.0013	0	0.0034	0.0035	0.0006	0.0011	0.4228	0.001	0	0.0001	0.0283	0.0154	0.1289	0	0.0001	0	0.0005	0.0328
426	233-1-209	12.096	0.289	0.0012	0.0007	0	0.0037	0.0043	0.0008	0.0011	0.076	0.0007	0	0.0279	0.0103	0.0117	0.0075	0	0	0	0	0
427	239-1-210	11.406	0.287	0.0012	0.0016	0	0.0039	0.0043	0.0004	0.0015	0.0145	0.0007	0.0005	0.0003	0.0142	0.0108	0.0809	0	0	0	0.0003	0.0692
428	251-1-211	11.462	0.287	0.0013	0.0653	0	0.0037	0.0045	0.0001	0.001	0.0122	0.0007	0.0005	0.0002	0.0121	0.0109	0.0934	0	0	0	0.0001	0.0349
429	260-1-212	11.602	0.593	0.0012	0.0051	0	0.0039	0.0052	0.0002	0.0016	0.0182	0.0007	0.0006	0.0002	0.0194	0.011	0.0974	0	0	0	0.0005	0.0414
430	267-1-213	11.705	0.297	0.001	0.0016	0	0.0036	0.0038	0.0002	0.0008	0.0103	0.0007	0	0.0001	0.0104	0.0105	0.0298	0	0	0	0.0001	0.0247
431	269-1-214	11.437	0.29	0.0011	0.0017	0	0.0036	0.0044	0.0012	0.0007	0.0039	0.0008	0.0001	0.0001	0.0038	0.0107	0.0568	0	0	0	0	0.0194
432	275-1-215	12.078	0.287	0.0012	0.0018	0	0.0037	0.0043	0.0005	0.001	0.3175	0.0008	0.0002	0.0001	0.0177	0.0139	0.0698	0	0	0	0.0002	0.0355
433	289-1-216	12.364	0.537	0.0019	0.1105	0	0.0044	0.0207	0.0006	0.003	0.0628	0.0008	0.0009	0.0001	0.0095	0.011	0.0038	0	0	0	0.0001	0.0261
434	207-1-217	9.9689	0.242	0.0009	0.001	0	0.0034	0.0031	0.0002	0.0009	0.1652	0.0008	0	0.0185	0.0185	0.0128	0.0565	0	0	0	0.0002	0

	SAMPLE	Silicon	Iron	Copper	Magnesium	Zinc	Nickel	Manganese	Lead	Chromium	Titanium	Tin	Calcium	Sodium	Vanadium	Gallium	Boron	Lithium	Berillium	Bismuth	Zirconium	Strontium
	#	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
435	210-1-218	9.9532	0.221	0.0007	0.0017	0	0.003	0.0032	0.0005	0.0011	0.1854	0.0009	0	0.0001	0.0178	0.012	0.0655	0	0	0	0.0003	0.0278
436	272-1-219	11.626	0.666	0.0014	0.1031	0	0.0039	0.5031	0.001	0.0007	0.0021	0.0011	0	0	0.0019	0.0106	0.0338	0	0	0	0	0.0131
437	240-1-220	11.924	0.299	0.001	0.0025	0	0.0037	0.0102	0.0005	0.0008	0.0096	0.0008	0.0001	0	0.009	0.0104	0.0334	0	0	0	0	0.0384
438	258-1-221	12.187	0.303	0.0037	0.0049	0	0.0036	0.4942	0.0015	0.0012	0.0998	0.0011	0.0003	0.0005	0.0109	0.0115	0.0154	0	0	0	0.0001	0.0233
439	213-1-222	12.242	0.29	0.0014	0.0015	0	0.0038	0.0103	0.001	0.0016	0.2319	0.0009	0	0.0143	0.0258	0.0131	0.0731	0	0	0	0.0004	0
440	219-1-223	12.703	0.295	0.0019	0.0023	0	0.0038	0.0091	0.001	0.0022	0.2082	0.0009	0.001	0.014	0.0235	0.0124	0.0645	0	0	0	0.0005	0.0011
441	222-1-224	12.88	0.293	0.0022	0.0027	0	0.0038	0.0088	0.0025	0.0022	0.2261	0.001	0.0019	0.0002	0.0233	0.0123	0.0672	0	0	0	0.0005	0.0374
442	225-1-225	12.065	0.291	0.0012	0.0021	0	0.0037	0.0048	0.0012	0.0014	0.2029	0.0009	0.0008	0.0005	0.0218	0.0124	0.0622	0	0	0	0.0004	0.001
443	228-1-226	12.331	0.294	0.0012	0.0018	0	0.0038	0.0051	0.0008	0.0016	0.1769	0.0009	0.0002	0.0058	0.0193	0.0121	0.0533	0	0	0	0.0003	0.0001
444	233-1-227	12.292	0.287	0.0014	0.0007	0	0.0036	0.0045	0.0006	0.0009	0.0807	0.0008	0	0.0246	0.0103	0.0115	0.0102	0	0	0	0	0
445	234-1-228	12.891	0.289	0.0018	0.001	0	0.0036	0.0069	0.0003	0.0014	0.0099	0.0007	0.0003	0.033	0.009	0.0108	0.0001	0	0	0	0	0.0008
446	231-1-229	12.51	0.288	0.0014	0.0014	0	0.0037	0.0048	0.0006	0.0017	0.2042	0.0009	0.0003	0.0155	0.0234	0.0127	0.0642	0	0	0	0.0004	0
447	237-1-230	12.179	0.291	0.0012	0.0023	0	0.0036	0.0048	0.0018	0.0017	0.2821	0.0011	0.0007	0.0007	0.028	0.0132	0.0876	0	0	0.0001	0.0005	0.0171
448	240-1-231	12.278	0.297	0.0013	0.0022	0	0.0035	0.0047	0.0007	0.0007	0.1424	0.0009	0.0009	0.0008	0.0122	0.0116	0.029	0	0	0	0.0001	0.0538
449	250-1-232	12.142	0.29	0.0012	0.0876	0	0.0035	0.0053	0.0009	0.0012	0.2433	0.001	0.0007	0.0001	0.0252	0.0128	0.0751	0	0	0	0.0005	0.053
450	251-1-233	11.756	0.284	0.0012	0.004	0	0.0036	0.0047	0.0009	0.0014	0.0252	0.0009	0.0011	0.0002	0.02	0.0105	0.0668	0	0	0	0.0006	0.0493
451	253-1-234	12.344	0.287	0.0012	0.1026	0	0.0037	0.0048	0.0018	0.0013	0.2331	0.001	0.0003	0.0001	0.0258	0.0129	0.0736	0	0	0	0.0005	0.0237
452	256-1-235	12.298	0.297	0.0012	0.0028	0	0.0039	0.1766	0.0011	0.0019	0.2039	0.0011	0.0005	0.0002	0.0235	0.0125	0.0644	0	0	0	0.0004	0.0367
453	289-1-236	12.756	0.706	0.002	0.1027	0.0004	0.0052	0.523	0.003	0.0044	0.0941	0.0012	0.0017	0.0007	0.0109	0.0114	0.015	0	0	0	0.0001	0.0299
454	259-1-237	12.128	0.3	0.002	0.0027	0	0.0041	0.51	0.0012	0.0023	0.1595	0.0012	0.0001	0.0001	0.0173	0.0123	0.0482	0	0	0	0.0002	0.0352
455	260-1-238	11.696	0.603	0.0014	0.002	0	0.0039	0.0116	0.0002	0.0012	0.0129	0.001	0.0004	0.0001	0.0118	0.0106	0.0595	0	0	0	0.0002	0.0357
456	281-1-239	11.955	0.598	0.0013	0.1158	0	0.0048	0.471	0.0019	0.0042	0.5321	0.0014	0.0002	0.0002	0.0391	0.0163	0.1477	0	0.0001	0.0002	0.0006	0.033
457	262-1-240	12.096	0.641	0.0016	0.0029	0	0.0042	0.0179	0.0006	0.0024	0.2271	0.0012	0.0002	0.0001	0.0228	0.0128	0.0721	0	0	0	0.0005	0.0332
458	265-1-241	12.109	0.61	0.0015	0.1079	0	0.004	0.5233	0.0011	0.0015	0.1474	0.0012	0.0003	0.0003	0.0171	0.0125	0.0437	0	0	0	0.0001	0.0295
459	277-1-242	12.292	0.291	0.0012	0.0019	0	0.0036	0.0048	0.0005	0.0009	0.1753	0.0011	0.0002	0.0002	0.0197	0.012	0.0552	0	0	0	0.0003	0.0543
460	275-1-243	12.287	0.278	0.0012	0.0019	0	0.0036	0.0047	0.0007	0.0008	0.3427	0.0011	0.0008	0.0001	0.017	0.0138	0.0753	0	0	0	0.0001	0.0374
461	276-1-244	12.524	0.292	0.0012	0.0017	0	0.0038	0.0045	0.0011	0.0015	0.2755	0.0011	0.0003	0	0.0236	0.0131	0.0785	0	0	0	0.0004	0.0415
462	279-1-245	12.102	0.628	0.0013	0.0513	0	0.0039	0.5028	0.0016	0.0014	0.2471	0.0013	0.0006	0.0002	0.0153	0.0134	0.0523	0	0	0	0.0001	0.0304
463	280-1-246	12.314	0.67	0.0013	0.0775	0	0.004	0.5213	0.0013	0.0017	0.182	0.0013	0.0006	0.0001	0.0208	0.0127	0.0521	0	0	0	0.0003	0.0321
464	282-1-247	12.582	0.31	0.0012	0.0026	0	0.0035	0.017	0.0006	0.0008	0.0237	0.001	0.0004	0.0001	0.0104	0.0104	0.0126	0	0	0	0.0001	0.0258
465	284-1-248	12.302	0.295	0.0014	0.0019	0	0.0037	0.0056	0.0007	0.0013	0.1535	0.0011	0.0002	0.0001	0.0171	0.0118	0.0462	0	0	0	0.0003	0.0413
466	283-1-249	12.384	0.296	0.0013	0.0021	0	0.0037	0.0052	0.0009	0.0017	0.1827	0.0011	0.0005	0.0002	0.039	0.0121	0.0736	0	0.0001	0	0.0012	0.0369
467	286-1-250	12.437	0.302	0.0013	0.0021	0	0.0037	0.0055	0.0006	0.0011	0.0331	0.001	0.0004	0.0002	0.0143	0.0103	0.0261	0	0	0	0.0003	0.0366
468	287-1-251	12.455	0.3	0.0012	0.0021	0	0.0036	0.0048	0.0005	0.0012	0.0964	0.0011	0.0003	0	0.0236	0.0112	0.0446	0	0	0	0.0007	0.0316
469	293-1-252	12.427	0.293	0.0012	0.0996	0	0.0037	0.5248	0.0013	0.001	0.1431	0.0012	0.0002	0.0001	0.0131	0.0121	0.0288	0	0	0	0.0001	0.0281
470	291-1-253	12.249	0.668	0.0013	0.0029	0	0.004	0.5642	0.0014	0.0013	0.1976	0.0014	0.0005	0.0001	0.0142	0.0128	0.0438	0	0	0	0.0001	0.0407
471	292-1-254	12.396	0.649	0.0013	0.1086	0	0.004	0.0145	0.0006	0.0012	0.1522	0.0011	0.0002	0.0001	0.0123	0.0121	0.0287	0	0	0	0.0001	0.0312
472	234-1-255	12.137	0.277	0.0012	0.0017	0	0.0043	0.0117	0.0013	0.0037	0.4412	0.001	0.0003	0.0215	0.0461	0.0154	0.1354	0	0.0001	0.0012	0.0009	0
473	237-1-256	12.37	0.298	0.0011	0.0019	0	0.0037	0.009	0.0009	0.0012	0.1692	0.0011	0	0.0001	0.0202	0.012	0.0533	0	0	0	0.0004	0.0114
474	251-1-257	11.946	0.288	0.0011	0.1072	0	0.004	0.0046	0.0008	0.0016	0.0182	0.0009	0.0002	0.0003	0.018	0.0109	0.0675	0	0	0	0.0004	0.046
475	256-1-258	12.268	0.288	0.0011	0.0028	0	0.0038	0.2061	0.0011	0.0014	0.2716	0.0012	0.0001	0.0001	0.028	0.0133	0.0919	0	0	0	0.0005	0.0798
476	259-1-259	12.153	0.285	0.001	0.0018	0.0019	0.0038	0.5048	0.0019	0.0016	0.3439	0.0013	0.0002	0.0001	0.3663	0.0143	0.1083	0	0.0001	0.0013	0.0006	0.0713
477	260-1-260	11.7	0.585	0.001	0.0017	0.0016	0.0038	0.0291	0.0005	0.001	0.0165	0.001	0.0001	0.0001	0.0145	0.0107	0.048	0	0	0.001	0.0003	0.0135
478	281-1-261	12.002	0.549	0.001	0.1039	0.0015	0.0041	0.5586	0.0013	0.0017	0.1458	0.0013	0	0	0.0177	0.0123	0.0485	0	0	0.0012	0.0002	0.0205
479	234-1-262	12.202	0.284	0.0011	0.001	0	0.0334	0.0043	0.0018	0.0017	0.0651	0.0008	0	0.032	0.0115	0.0114	0.018	0	0	0	0	0
480	251-1-263	12.022	0.306	0.0011	0.1205	0	0.0037	0.0051	0.0007	0.0007	0.0017	0.0008	0.0001	0.0001	0.002	0.0105	0.0302	0	0	0	0	0.0138
481	256-1-264	12.041	0.306	0.0012	0.0031	0	0.0041	0.2412	0.0005	0.0024	0.071	0.001	0	0	0.0105	0.0109	0.0199	0	0	0	0.0001	0.0175
482	259-1-265	12.128	0.304	0.001	0.0032	0	0.0035	0.5466	0.0009	0.0006	0.0705	0.0011	0.0001	0.0002	0.0113	0.011	0.0174	0	0	0	0.0001	0.0176
483	275-1-266	12.047	0.298	0.0011	0.0017	0	0.0037	0.0163	0.0003	0.0012	0.104	0.0009	0	0	0.0106	0.0112	0.0129	0	0	0	0.0001	0.0164

	SAMPLE	Silicon	Iron	Copper	Magnesium	Zinc	Nickel	Manganese	Lead	Chromium	Titanium	Tin	Calcium	Sodium	Vanadium	Gallium	Boron	Lithium	Berillium	Bismuth	Zirconium	Strontium
	#	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
484	276-1-267	12.17	0.298	0.0011	0.0017	0	0.0037	0.0049	0.0003	0.0011	0.0874	0.0009	0	0	0.0108	0.011	0.0166	0	0	0	0.0001	0.0177
485	279-1-268	12.014	0.652	0.0017	0.105	0	0.0041	0.5321	0.0011	0.0018	0.1192	0.0012	0	0	0.0115	0.012	0.0179	0	0	0	0.0001	0.018
486	294-1-269	12.297	0.305	0.001	0.0019	0	0.0037	0.0045	0.0026	0.0013	0.0224	0.001	0	0	0.0091	0.0102	0.0013	0	0	0	0.0001	0.0153
487	RM10	11.473	0.409	0.0153	0.0948	0.022	0.002	0.2965	0.001	0.0014	0.1127	0.0009	0.0002	0.0016	0.0053	0.0104	0	0	0	0	0	0.0166
488	RM11	11.574	0.435	0.0034	0.0743	0	0.0023	0.2919	0.0009	0.0006	0.1149	0.0009	0.0001	0.0025	0.0061	0.0114	0	0	0	0	0	0.0121
489	HAM1	12.849	0.106	0.0009	0.0009	0	0.0013	0.0023	0	0.0001	0.0146	0.0007	0.0001	0.0129	0.0054	0.0085	0.0001	0	0	0	0	0
490	AX65	12.746	0.118	0.0054	0.0009	0	0.0019	0.0021	0	0.0001	0.0256	0.0007	0.0001	0.012	0.0091	0.0099	0.0002	0	0	0	0	0
491	RMF	12.461	0.371	0.0018	0.0275	0	0.0038	0.1298	0.0027	0.0015	0.0391	0.001	0.0004	0.0004	0.006	0.0106	0.0113	0	0	0	0	0.0515
492	RMG	11.622	0.391	0.0392	0.0507	0.0035	0.0036	0.1395	0.0015	0.0027	0.0147	0.0011	0.0001	0.0003	0.0018	0.0105	0.0107	0	0	0	0	0.0228
493	RMX	11.043	0.428	0.2677	0.0247	0.0012	0.0031	0.2578	0.004	0.0006	0.0803	0.0024	0.0002	0.0003	0.0077	0.0113	0.0021	0	0	0	0	0.0435
494	RMY	12.061	0.223	0.0049	0.014	0.0002	0.0022	0.0872	0.0015	0.001	0.0511	0.0009	0	0.0006	0.0066	0.0099	0.0086	0	0	0	0.0001	0.0207
495	RMZ	11.541	0.291	0.0058	0.0218	0	0.0029	0.0955	0.0026	0	0.0082	0.0009	0	0.0007	0.0007	0.0095	0.0104	0	0	0	0	0.0223

Appendix I

AFS Modification Results

	Sample	Modification Observation				
	#	1	2	3	AVE.	STD. DEV.
1	37-1-2.	6	5	3.5	4.83333	1.2583057
2	43-2-2.	4	4	5	4.33333	0.5773503
3	44-3-2.	1	1	1	1	0
4	48-4-2.	0.5	0.5	0.5	0.5	0
5	61-1-3.	4	4.5	3.5	4	0.5
6	67-2-3.	1.5	2	1	1.5	0.5
7	68-3-3.	1	1	1	1	0
8	72-4-3.	1	1	1	1	0
9	1-1-4.	6	6	6	6	0
10	7-2-4.	6	6	6	6	0
11	8-3-4.	5	4.5	5	4.83333	0.2886751
12	12-4-4.	3.5	3	2.5	3	0.5
13	109-1-5.	5	5	4.5	4.83333	0.2886751
14	120-2-5.	3	3	2	2.66667	0.5773503
15	97-1-6.	4	5	4.5	4.5	0.5
16	108-2-6.	4	2	3	3	1
17	169-1-7.	0.5	0.5	0.5	0.5	0
18	170-2-7.	2	1	2	1.66667	0.5773503
19	171-3-7.	2	1.5	1.5	1.66667	0.2886751
20	172-4-7.	6	5	5	5.33333	0.5773503
21	188-1-8.	4	4	4	4	0
22	189-2-8.	7	6	7	6.66667	0.5773503
23	190-3-8.	7	7	7	7	0
24	191-4-8.	6	7.5	8	7.16667	1.040833
25	180-1-9.	5	3	3	3.66667	1.1547005
26	181-2-9.	2	3	4	3	1
27	182-3-9.	4	5	2	3.66667	1.5275252
28	183-4-9.	2	3	5	3.33333	1.5275252
29	204-1-10.	1.5	2	1.5	1.66667	0.2886751
30	205-2-10.	1.5	2	1.5	1.66667	0.2886751
31	1-1-11.	3	4.5	3	3.5	0.8660254
32	7-2-11.	4	2.5	3	3.16667	0.7637626
33	9-3-11.	1.5	1.5	1.5	1.5	0
34	11-4-11.	1	1.5	3	1.83333	1.040833
35	2-1-12.	4	4	4.5	4.16667	0.2886751
36	4-2-12.	1.5	1.5	1	1.33333	0.2886751
37	6-3-12.	1.5	1.5	1	1.33333	0.2886751
38	12-4-12.	1	1	1	1	0
39	3-1-13.	1.5	2	1.5	1.66667	0.2886751
40	5-2-13.	1	1	1	1	0
41	8-1-14.	1.5	1.5	1.5	1.5	0

	Sample	Modification Observation				
	#	1	2	3	AVE.	STD. DEV.
42	10-2-14.	1	1.5	1	1.16667	0.2886751
43	37-1-15.	1	1	1	1	0
44	43-2-15.	1.5	1.5	1.5	1.5	0
45	45-3-15.	1	1	1	1	0
46	47-4-15.	1.5	1	1.5	1.33333	0.2886751
47	38-1-16.	1	1	1	1	0
48	40-2-16.	1	1	1	1	0
49	42-3-16.	1.5	1.5	1.5	1.5	0
50	48-4-16.	1.5	1.5	1.5	1.5	0
51	39-1-17.	1	1.5	1.5	1.33333	0.2886751
52	41-2-17.	1	1	1.5	1.16667	0.2886751
53	44-1-18.	1.5	1	1	1.16667	0.2886751
54	46-2-18.	1	2	1.5	1.5	0.5
55	73-1-19.	4.5	5	4	4.5	0.5
56	79-2-19.	5	4	4	4.33333	0.5773503
57	81-3-19.	3	2.5	2.5	2.66667	0.2886751
58	83-4-19.	3	4	3	3.33333	0.5773503
59	74-1-20.	3.5	4	3	3.5	0.5
60	76-2-20.	1.5	1	1.5	1.33333	0.2886751
61	78-3-20.	1.5	1.5	1.5	1.5	0
62	84-4-20.	2	3	2	2.33333	0.5773503
63	75-1-21.	3	1	3	2.33333	1.1547005
64	77-2-21.	1	2	1	1.33333	0.5773503
65	80-1-22.	2.5	1.5	2	2	0.5
66	82-2-22.	2.5	2	0	1.5	1.3228757
67	110-1-23.	2	4	5	3.66667	1.5275252
68	112-2-23.	1	2	2	1.66667	0.5773503
69	114-3-23.	1	3	1	1.66667	1.1547005
70	120-4-23.	2	2	2	2	0
71	10-1-24.	4	6	5	5	1
72	12-2-24.	4	4	4	4	0
73	118-1-25.	4	4	3.5	3.83333	0.2886751
74	120-2-25.	3.5	4	2.5	3.33333	0.7637626
75	79-1-26.	4	4	4	4	0
76	81-2-26.	3	2	3	2.66667	0.5773503
77	83-3-26.	3	2	2.5	2.5	0.5
78	84-4-26.	2	3	2	2.33333	0.5773503
79	159-1-27.	5	2	5	4	1.7320508
80	195-2-27.	3	3	5	3.66667	1.1547005
81	4-1-28.	5	3	5	4.33333	1.1547005
82	12-2-28.	3	3	3	3	0

	Sample	Modification Observation				
	#	1	2	3	AVE.	STD. DEV.
83	157-1-29.	2	5	5	4	1.7320508
84	160-2-29.	2	4	5	3.66667	1.5275252
85	77-1-30.	3.5	5	3	3.83333	1.040833
86	84-2-30.	3	5	3	3.66667	1.1547005
87	109-1-31.	4	4	3	3.66667	0.5773503
88	115-2-31.	3	3	2.5	2.83333	0.2886751
89	117-3-31.	3.5	4	2	3.16667	1.040833
90	120-4-31.	4	4	3	3.66667	0.5773503
91	38-1-32.	4	4.5	5	4.5	0.5
92	40-2-32.	2.5	6	6	4.83333	2.0207259
93	46-3-32.	3	3	3	3	0
94	48-4-32.	3	4	4	3.66667	0.5773503
95	1-1-33.	4.5	6	4.5	5	0.8660254
96	2-2-33.	6	6	6	6	0
97	6-3-33.	4	5	6	5	1
98	12-4-33.	5	6	5	5.33333	0.5773503
99	3-1-34.	6	5	6	5.66667	0.5773503
100	5-2-34.	6	5	5	5.33333	0.5773503
101	7-1-35.	5	5	5	5	0
102	9-2-35.	5	6	5	5.33333	0.5773503
103	8-1-36.	4	6	5	5	1
104	24-2-36.	6	5	4	5	1
105	11-1-37.	5	5	5	5	0
106	35-2-37.	6	4	5	5	1
107	123-1-38.	3	4	4	3.66667	0.5773503
108	135-2-38.	3	4.5	5	4.16667	1.040833
109	143-3-38.	3	5	4	4	1
110	144-4-38.	2	4	4	3.33333	1.1547005
111	37-1-39.	5	5.5	3.5	4.66667	1.040833
112	39-2-39.	3	5	6	4.66667	1.5275252
113	41-3-39.	6	3	4	4.33333	1.5275252
114	42-4-39.	4	6	5	5	1
115	43-1-40.	3	4	5	4	1
116	44-2-40.	3	5	5	4.33333	1.1547005
117	45-1-41.	4	5	4	4.33333	0.5773503
118	47-2-41.	3	5	6	4.66667	1.5275252
119	74-1-42.	4	5	4	4.33333	0.5773503
120	76-2-42.	5	6	7	6	1
121	78-3-42.	7	6	4	5.66667	1.5275252
122	84-4-42.	4	5	5	4.66667	0.5773503
123	75-1-43.	6	7	5	6	1

	Sample	Modification Observation				
	#	1	2	3	AVE.	STD. DEV.
124	81-2-43.	3	2.5	2.5	2.66667	0.2886751
125	79-1-44.	4	4	4	4	0
126	80-2-44.	3	5	5	4.33333	1.1547005
127	82-1-45.	3	5	3.5	3.83333	1.040833
128	94-2-45.	3	4	3.5	3.5	0.5
129	83-1-46.	6	4	3	4.33333	1.5275252
130	95-2-46.	3.5	4	4.5	4	0.5
131	110-1-47.	2	5	5	4	1.7320508
132	112-2-47.	3	6	5.5	4.83333	1.6072751
133	114-3-47.	2.5	5	3	3.5	1.3228757
134	120-4-47.	4	4.5	5	4.5	0.5
135	111-1-48.	2.5	6	4	4.16667	1.7559423
136	113-2-48.	5.5	5	3	4.5	1.3228757
137	116-1-49.	2	5	5	4	1.7320508
138	118-2-49.	3	5	4	4	1
139	145-1-50.	7	5	5	5.66667	1.1547005
140	147-2-50.	6	6.5	7	6.5	0.5
141	151-1-51.	3	5	5	4.33333	1.1547005
142	155-2-51.	3	5	5.5	4.5	1.3228757
143	158-1-52.	2	6	6	4.66667	2.3094011
144	160-2-52.	1.5	5	6	4.16667	2.3629078
145	164-1-53.	2	6	6	4.66667	2.3094011
146	168-2-53.	4	5	5	4.66667	0.5773503
147	149-1-54.	4	4	5	4.33333	0.5773503
148	150-2-54.	1.5	6	6	4.5	2.5980762
149	165-1-55.	3	4.5	5.5	4.33333	1.2583057
150	166-2-55.	3	5	5.5	4.5	1.3228757
151	163-1-56.	3.5	5	5.5	4.66667	1.040833
152	167-2-56.	4	5	5.5	4.83333	0.7637626
153	152-1-57.	5.5	5	7	5.83333	1.040833
154	156-2-57.	5	7	5	5.66667	1.1547005
155	13-1-58.	6	7	6	6.33333	0.5773503
156	15-2-58.	5	5	6	5.33333	0.5773503
157	17-3-58.	3.5	5	5.5	4.66667	1.040833
158	23-4-58.	4	5.5	5	4.83333	0.7637626
159	19-1-59.	5	5	5.5	5.16667	0.2886751
160	21-2-59.	3	5.5	5.5	4.66667	1.4433757
161	26-1-60.	7	5	5.5	5.83333	1.040833
162	28-2-60.	3.5	5.5	5	4.66667	1.040833
163	30-3-60.	3	5	5	4.33333	1.1547005
164	36-4-60.	3	5.5	5.5	4.66667	1.4433757
165	68-1-61.	3	5	5	4.33333	1.1547005
166	70-2-61.	4	4	4.5	4.16667	0.2886751
167	146-1-62.	4	5	3	4	1
168	148-2-62.	3.5	5	5	4.5	0.8660254
169	153-1-63.	4	4	5	4.33333	0.5773503
170	154-2-63.	4	5	5	4.66667	0.5773503
171	161-1-64.	4	5	5	4.66667	0.5773503

	Sample	Modification Observation				
	#	1	2	3	AVE.	STD. DEV.
172	162-2-64.	3.5	5	4	4.16667	0.7637626
173	147-1-65.	4	5	4.5	4.5	0.5
174	155-2-65.	3	4	5	4	1
175	32-1-66.	4	5	6	5	1
176	34-2-66.	5	5	5	5	0
177	31-1-67.	3.5	5	5	4.5	0.8660254
178	33-2-67.	3	4	5	4	1
179	20-1-68.	2.5	5	4	3.83333	1.2583057
180	22-2-68.	3	5	4	4	1
181	14-1-69.	4	5	5	4.66667	0.5773503
182	18-2-69.	5	4	5	4.66667	0.5773503
183	25-1-70.	4	5.5	5	4.83333	0.7637626
184	27-2-70.	5	5	5.5	5.16667	0.2886751
185	29-3-70.	4	5	5	4.66667	0.5773503
186	35-4-70.	4	5	4.5	4.5	0.5
187	49-1-72.	3	5	5	4.33333	1.1547005
188	51-2-72.	2.5	4.5	5	4	1.3228757
189	53-3-72.	2	4.5	4.5	3.66667	1.4433757
190	59-4-72.	4.5	4	4.5	4.33333	0.2886751
191	55-1-73.	4	4.5	5	4.5	0.5
192	57-2-73.	3	4.5	5	4.16667	1.040833
193	50-1-74.	4.5	5	5	4.83333	0.2886751
194	52-2-74.	3	5	5	4.33333	1.1547005
195	54-3-74.	5	5	5	5	0
196	60-4-74.	2.5	3	3.5	3	0.5
197	56-1-75.	4	5	4.5	4.5	0.5
198	58-2-75.	3.5	5	4.5	4.33333	0.7637626
199	61-1-76.	2.5	4.5	5	4	1.3228757
200	63-2-76.	3	5	5	4.33333	1.1547005
201	65-3-76.	3.5	5	5	4.5	0.8660254
202	71-4-76.	3.5	5	5	4.5	0.8660254
203	67-1-77.	2.5	5	5.5	4.33333	1.6072751
204	69-2-77.	3	4.5	5	4.16667	1.040833
205	62-1-78.	3.5	5	5	4.5	0.8660254
206	64-2-78.	3	5.5	5	4.5	1.3228757
207	66-3-78.	5	5	5	5	0
208	72-4-78.	3	4.5	4.5	4	0.8660254
209	85-1-79.	7	5.5	5	5.83333	1.040833
210	87-2-79.	7	5.5	5	5.83333	1.040833
211	89-3-79.	7	5.5	4.5	5.66667	1.2583057
212	95-4-79.	7	4	4	5	1.7320508
213	91-1-80.	4	4	3.5	3.83333	0.2886751
214	93-2-80.	2.5	4	3.5	3.33333	0.7637626
215	86-1-81.	7	6.5	5	6.16667	1.040833
216	88-2-81.	4	4.5	3.5	4	0.5
217	90-3-81.	7	7	5	6.33333	1.1547005
218	96-4-81.	4	4	5	4.33333	0.5773503
219	92-1-82.	3	7	4	4.66667	2.081666

	Sample	Modification Observation				
	#	1	2	3	AVE.	STD. DEV.
220	94-2-82.	4	3.5	3	3.5	0.5
221	97-1-83.	7	7	8	7.33333	0.5773503
222	99-2-83.	7	4	7	6	1.7320508
223	101-3-83.	7	7.5	7	7.16667	0.2886751
224	107-4-83.	4.5	6.5	7.5	6.16667	1.5275252
225	103-1-84.	3.5	5.5	8	5.66667	2.2546249
226	105-2-84.	5	4	4	4.33333	0.5773503
227	98-1-85.	7	6	7	6.66667	0.5773503
228	100-2-85.	7	7	7	7	0
229	102-3-85.	6	7	7	6.66667	0.5773503
230	108-4-85.	6	7	5	6	1
231	104-1-86.	4	4	4.5	4.16667	0.2886751
232	106-2-86.	4	7	7	6	1.7320508
233	121-1-87.	4.5	4.5	4	4.33333	0.2886751
234	123-2-87.	5.5	5	3.5	4.66667	1.040833
235	125-3-87.	3	5	4.5	4.16667	1.040833
236	131-4-87.	3	4	3.5	3.5	0.5
237	128-1-88.	3.5	3	3.5	3.33333	0.2886751
238	130-2-88.	3	4	4	3.66667	0.5773503
239	122-1-89.	3.5	4	5	4.16667	0.7637626
240	124-2-89.	3	4	5	4	1
241	126-3-89.	3	5	5	4.33333	1.1547005
242	132-4-89.	3.5	5	4.5	4.33333	0.7637626
243	127-1-90.	4	4	4	4	0
244	129-2-90.	3	4	4	3.66667	0.5773503
245	133-1-91.	3	4	5	4	1
246	137-2-91.	4.5	4	5	4.5	0.5
247	139-1-92.	3	3	3	3	0
248	141-2-92.	4	3.5	3.5	3.66667	0.2886751
249	140-1-93.	3.5	3.5	3.5	3.5	0
250	142-2-93.	4	3	3	3.33333	0.5773503
251	131-1-94.	6	5.5	4	5.16667	1.040833
252	136-2-94.	3	5	5	4.33333	1.1547005
253	138-3-94.	5	4.5	4	4.5	0.5
254	144-4-94.	3.5	3.5	3.5	3.5	0
255	169-1-95.	1	1	1	1	0
256	170-2-95.	2	2	1.5	1.83333	0.2886751
257	171-1-96.	3.5	4	4.5	4	0.5
258	172-2-96.	1.5	5	4.5	3.66667	1.8929694
259	200-1-97.	3.5	4	3	3.5	0.5
260	201-2-97.	6.5	6	7	6.5	0.5
261	199-1-98.	1.5	1	1	1.16667	0.2886751
262	203-2-98.	3	4.5	5	4.16667	1.040833
263	177-1-99.	1	1.5	4.5	2.33333	1.8929694
264	178-2-99.	1.5	4	5	3.5	1.8027756
265	179-1-100	4	5	5	4.66667	0.5773503
266	181-2-100	3	4	4	3.66667	0.5773503
267	197-1-101	2	1.5	5	2.83333	1.8929694

	Sample	Modification Observation				
	#	1	2	3	AVE.	STD. DEV.
268	198-2-101	2.5	4.5	5	4	1.3228757
269	185-1-102	4	5	5	4.66667	0.5773503
270	186-2-102	4.5	3	4	3.83333	0.7637626
271	14-1-103.	5	5	5	5	0
272	18-2-103.	3.5	4.5	5	4.33333	0.7637626
273	16-1-104.	7	5.5	5.5	6	0.8660254
274	22-2-104.	5	5	3	4.33333	1.1547005
275	57-1-105.	4	5	3.5	4.16667	0.7637626
276	58-2-105.	3	4.5	4.5	4	0.8660254
277	52-1-106.	3.5	5	5	4.5	0.8660254
278	70-2-106.	4	5	5	4.66667	0.5773503
279	25-1-107.	7	6	6	6.33333	0.5773503
280	31-2-107.	4	4	5	4.33333	0.5773503
281	50-1-108.	4.5	5.5	5	5	0.5
282	58-2-108.	3.5	3	2.5	3	0.5
283	57-1-109.	3	3.5	4	3.5	0.5
284	71-2-109.	3	4	4.5	3.83333	0.7637626
285	91-1-110.	3.5	3.5	4	3.66667	0.2886751
286	93-2-110.	7	7	2.5	5.5	2.5980762
287	173-1-111	1	5	5	3.66667	2.3094011
288	174-2-111	4	7	6.5	5.83333	1.6072751
289	182-1-112	5	5	4.5	4.83333	0.2886751
290	183-2-112	4.5	4	5	4.5	0.5
291	185-1-113	2	2	2.5	2.16667	0.2886751
292	186-2-113	4	5	3	4	1
293	175-1-114	7.5	7	8	7.5	0.5
294	176-2-114	8	8	7	7.66667	0.5773503
295	180-1-115	3.5	5	5	4.5	0.8660254
296	182-2-115	3	5.5	5.5	4.66667	1.4433757
297	189-1-116	7	7	6	6.66667	0.5773503
298	190-2-116	8	8	8	8	0
299	192-1-117	2	2.5	1.5	2	0.5
300	193-2-117	1.5	3.5	4	3	1.3228757
301	194-1-118	4	4	2.5	3.5	0.8660254
302	195-2-118	2	5	5.5	4.16667	1.8929694
303	197-1-119	3	2	5	3.33333	1.5275252
304	198-2-119	3.5	4	2	3.16667	1.040833
305	154-1-120	7	7	7	7	0
306	191-2-120	7	7	7	7	0
307	92-1-121.	7	5	5	5.66667	1.1547005
308	108-2-121	4.5	4	4	4.16667	0.2886751
309	103-1-122	3.5	7	7	5.83333	2.0207259
310	107-2-122	4	5	6.5	5.16667	1.2583057
311	173-1-123	7	8	7.5	7.5	0.5
312	174-2-123	8	7	8	7.66667	0.5773503
313	41-1-124.	3	5	5	4.33333	1.1547005
314	60-2-124.	4	2	3	3	1
315	195-1-125	3.5	4	4	3.83333	0.2886751

	Sample	Modification Observation				
	#	1	2	3	AVE.	STD. DEV.
316	198-2-125	4	2	4	3.33333	1.1547005
317	184-1-126	1	1	1	1	0
318	189-2-126	7	8	8	7.66667	0.5773503
319	182-1-127	5	4	5	4.66667	0.5773503
320	183-2-127	5	3	4.5	4.16667	1.040833
321	180-1-128	3	5	4.5	4.16667	1.040833
322	164-2-128	3	4	4.5	3.83333	0.7637626
323	173-1-129	7	4	5	5.33333	1.5275252
324	146-2-129	2	7	5	4.66667	2.5166115
325	41-1-130.	3	5	5	4.33333	1.1547005
326	60-2-130.	3	3	2.5	2.83333	0.2886751
327	81-1-131.	7	5	6	6	1
328	288-2-131	3	3	3.5	3.16667	0.2886751
329	120-1-132	4	3	3.5	3.5	0.5
330	289-2-132	3	2	4	3	1
331	173-1-133	4	4	4.5	4.16667	0.2886751
332	153-2-133	7	7	5	6.33333	1.1547005
333	41-1-134.	4.5	5	5	4.83333	0.2886751
334	60-2-134.	1.5	4.5	4	3.33333	1.6072751
335	173-1-135	7	7	7	7	0
336	212-2-135	7	3	4	4.66667	2.081666
337	224-1-136	1	1.5	2	1.5	0.5
338	227-2-136	2	3	4	3	1
339	252-1-137	3	4	4	3.66667	0.5773503
340	289-2-137	1	1	4	2	1.7320508
341	261-1-138	2.5	5	5	4.16667	1.4433757
342	264-2-138	3.5	1	5	3.16667	2.0207259
343	218-1-139	5	4.5	7.5	5.66667	1.6072751
344	233-2-139	8	7.5	6	7.16667	1.040833
345	238-1-140	3	1.5	3.5	2.66667	1.040833
346	240-2-140	3	3	4.5	3.5	0.8660254
347	255-1-141	4	3	4.5	3.83333	0.7637626
348	258-2-141	3	4	5	4	1
349	274-1-142	5	2.5	3	3.5	1.3228757
350	278-2-142	2	3	3	2.66667	0.5773503
351	275-1-143	3	3	3	3	0
352	279-2-143	1.5	3	2	2.16667	0.7637626
353	276-1-144	2.5	4	5	3.83333	1.2583057
354	280-2-144	2	2.5	4	2.83333	1.040833
355	236-1-146	3.5	2.5	5	3.66667	1.2583057
356	264-2-146	2	4	3	3	1
357	28-1-148.	5	5.5	5.5	5.33333	0.2886751
358	60-1-149.	4	5	4	4.33333	0.5773503
359	32-1-150.	7	5	6	6	1
360	134-1-151	4.5	4.5	3.5	4.16667	0.5773503
361	215-1-152	5	3	1.5	3.16667	1.7559423
362	221-2-152	4	3	3.5	3.5	0.5
363	230-1-153	6	5	6	5.66667	0.5773503

	Sample	Modification Observation				
	#	1	2	3	AVE.	STD. DEV.
364	233-2-153	8	8	7	7.66667	0.5773503
365	206-1-154	2	4.5	6	4.16667	2.0207259
366	258-2-154	3.5	4	4.5	4	0.5
367	240-1-154	4	3	2.5	3.16667	0.7637626
368	209-1-155	4	3.5	3.5	3.66667	0.2886751
369	274-1-155	1.5	3	6	3.5	2.2912878
370	278-2-155	2	4	1.5	2.5	1.3228757
371	275-1-156	5	2	3	3.33333	1.5275252
372	221-1-156	5	1.5	1.5	2.66667	2.0207259
373	279-2-156	1	2	3	2	1
374	233-1-157	8	8	8	8	0
375	258-1-158	1	1	1	1	0
376	264-1-159	2.5	2.5	2.5	2.5	0
377	275-1-160	4	1	2.5	2.5	1.5
378	279-1-161	1.5	2	2	1.83333	0.2886751
379	292-1-162	1.5	2	2	1.83333	0.2886751
380	289-1-163	1	2	3.5	2.16667	1.2583057
381	293-1-164	2.5	4	4.5	3.66667	1.040833
382	278-1-165	2.5	4	3	3.16667	0.7637626
383	291-1-166	4	5	4	4.33333	0.5773503
384	283-1-167	2	2	2	2	0
385	169-1-168	1	1	1	1	0
386	233-1-169	8	7	7	7.33333	0.5773503
387	258-1-170	5	4	5	4.66667	0.5773503
388	277-1-171	3.5	3	2.5	3	0.5
389	269-1-172	4.5	5	3	4.16667	1.040833
390	269-1-173	1	1.5	1.5	1.33333	0.2886751
391	282-1-174	5	4.5	4.5	4.66667	0.2886751
392	205-1-175	7	5	5.5	5.83333	1.040833
393	278-1-176	2.5	3	1	2.16667	1.040833
394	169-1-177	1	1	1	1	0
395	207-1-178	5	6	6	5.66667	0.5773503
396	208-1-179	1.5	1	1	1.16667	0.2886751
397	211-1-180	5	5.5	6	5.5	0.5
398	214-1-181	3.5	5	4.5	4.33333	0.7637626
399	217-1-182	5	5	5	5	0
400	220-1-183	2	2.5	2.5	2.33333	0.2886751
401	225-1-184	1	1	1	1	0
402	207-1-185	7	5.5	5.5	6	0.8660254
403	211-1-186	5	4.5	4.5	4.66667	0.2886751
404	214-1-187	1	1	1	1	0
405	233-1-188	1	1	1	1	0
406	226-1-189	4	5.5	4	4.5	0.8660254
407	229-1-190	4	5.5	5	4.83333	0.7637626
408	232-1-191	8	7	7	7.33333	0.5773503
409	235-1-192	1	1	1	1	0
410	239-1-193	1.5	1	1.5	1.33333	0.2886751
411	251-1-194	1	1	1	1	0

	Sample	Modification Observation				
	#	1	2	3	AVE.	STD. DEV.
412	254-1-195	2	1	1	1.33333	0.5773503
413	257-1-196	1	2	2	1.66667	0.5773503
414	263-1-197	1.5	1.5	1.5	1.5	0
415	267-1-198	1	1.5	1.5	1.33333	0.2886751
416	273-1-199	1	1	1	1	0
417	260-1-200	1.5	1.5	1.5	1.5	0
418	233-1-201	7	8	6.5	7.16667	0.7637626
419	213-1-202	8	8	6.5	7.5	0.8660254
420	216-1-203	3	3.5	4.5	3.66667	0.7637626
421	285-1-204	4.5	4	4	4.16667	0.2886751
422	270-1-205	4	2	2.5	2.83333	1.040833
423	271-1-206	3	1	2	2	1
424	207-1-207	7	6	6.5	6.5	0.5
425	210-1-208	4	5.5	5	4.83333	0.7637626
426	233-1-209	8	5	8	7	1.7320508
427	239-1-210	1	2	1.5	1.5	0.5
428	251-1-211	1	1	1	1	0
429	260-1-212	2	1.5	1	1.5	0.5
430	267-1-213	2	2	2	2	0
431	269-1-214	1	2	2	1.66667	0.5773503
432	275-1-215	3.5	4	4.5	4	0.5
433	289-1-216	3	4	3.5	3.5	0.5
434	207-1-217	8	6	5	6.33333	1.5275252
435	210-1-218	3.5	3.5	4.5	3.83333	0.5773503
436	272-1-219	1	1	1	1	0
437	240-1-220	1.5	2	1.5	1.66667	0.2886751
438	258-1-221	4	3.5	5	4.16667	0.7637626
439	213-1-222	7	7	5.5	6.5	0.8660254

	Sample	Modification Observation				
	#	1	2	3	AVE.	STD. DEV.
440	219-1-223	8	7	6	7	1
441	222-1-224	4	5	5	4.66667	0.5773503
442	225-1-225	1	1	1	1	0
443	228-1-226	4.5	4	3.5	4	0.5
444	233-1-227	8	8	5	7	1.7320508
445	234-1-228	8	5.5	5.5	6.33333	1.4433757
446	231-1-229	8	5	5.5	6.16667	1.6072751
447	237-1-230	2	5	5	4	1.7320508
448	240-1-231	5	4.5	2	3.83333	1.6072751
449	250-1-232	3	4	4	3.66667	0.5773503
450	251-1-233	1	1.5	1.5	1.33333	0.2886751
451	253-1-234	1	3	1.5	1.83333	1.040833
452	256-1-235	3	4	5	4	1
453	289-1-236	3	1	1	1.66667	1.1547005
454	259-1-237	3.5	4.5	4.5	4.16667	0.5773503
455	260-1-238	1.5	2	2	1.83333	0.2886751
456	281-1-239	3	3.5	3	3.16667	0.2886751
457	262-1-240	4.5	4	5	4.5	0.5
458	265-1-241	2	1	2	1.66667	0.5773503
459	277-1-242	4.5	4.5	4.5	4.5	0
460	275-1-243	5	5	5	5	0
461	276-1-244	5	3.5	4.5	4.33333	0.7637626
462	279-1-245	3	4	5	4	1
463	280-1-246	3	3	3	3	0
464	282-1-247	3.5	3.5	5	4	0.8660254
465	284-1-248	4.5	4	3.5	4	0.5
466	283-1-249	3.5	4	5	4.16667	0.7637626
467	286-1-250	3	5	3.5	3.83333	1.040833

	Sample	Modification Observation				
	#	1	2	3	AVE.	STD. DEV.
468	287-1-251	3.5	4	5	4.16667	0.7637626
469	293-1-252	3	2	3	2.66667	0.5773503
470	291-1-253	4.5	5	4.5	4.66667	0.2886751
471	292-1-254	1.5	4	1.5	2.33333	1.4433757
472	234-1-255	8	7	6	7	1
473	237-1-256	1	2.5	2.5	2	0.8660254
474	251-1-257	1.5	1	1	1.16667	0.2886751
475	256-1-258	5	5	3.5	4.5	0.8660254
476	259-1-259	4.5	5.5	5	5	0.5
477	260-1-260	1.5	1	1.5	1.33333	0.2886751
478	281-1-261	2	2	3.5	2.5	0.8660254
479	234-1-262	8	8	7	7.66667	0.5773503
480	251-1-263	1.5	1	1	1.16667	0.2886751
481	256-1-264	4.5	3	4.5	4	0.8660254
482	259-1-265	3	4.5	5	4.16667	1.040833
483	275-1-266	3	4	5	4	1
484	276-1-267	3	5	5	4.33333	1.1547005
485	279-1-268	4	1.5	2.5	2.66667	1.2583057
486	294-1-269	4	3	3.5	3.5	0.5
487	RM10	3	3	4	3.33333	0.5773503
488	RM11	5	4	4.5	4.5	0.5
489	HAM1	6.5	6.5	5.5	6.16667	0.5773503
490	AX65	5	5	7	5.66667	1.1547005
491	RMF	2.5	3.5	4.5	3.5	1
492	RMG	3	4	4	3.66667	0.5773503
493	RMX	2.5	2	2	2.16667	0.2886751
494	RMY	3	4.5	4.5	4	0.8660254
495	RMZ	2	4	4.5	3.5	1.3228757

Appendix J

Porosity Quantification Results

	SAMPLE	Porosity Observation				
	#	1	2	3	AVE.	%AREA
1	37-1-2.	5	4.5	5	4.83	0.5677
2	43-2-2.	6	6	6	6.00	1.07
3	44-3-2.	3	3	3	3.00	0.19
4	48-4-2.	4.5	5	4.5	4.67	0.5373
5	61-1-3.	5	6	6	5.67	0.9149
6	67-2-3.	3.5	4	3.5	3.67	0.3374
7	68-3-3.	2	2	2	2.00	0.05
8	72-4-3.	5.5	6	6	5.83	0.9901
9	1-1-4.	4	4	5	4.33	0.4727
10	7-2-4.	5	6	5.5	5.50	0.835
11	8-3-4.	1	1	1	1.00	0
12	12-4-4.	1	1.5	1	1.17	0.0085
13	109-1-5.	4	4	5	4.33	0.4727
14	120-2-5.	4	5	4	4.33	0.4727
15	97-1-6.	2	1.5	2	1.83	0.0415
16	108-2-6.	5	6	5	5.33	0.7551
17	169-1-7.	1	1	1.5	1.17	0.0085
18	170-2-7.	1	1	1.5	1.17	0.0085
19	171-3-7.	1	1	1.5	1.17	0.0085
20	172-4-7.	3.5	4	5	4.17	0.4423
21	188-1-8.	4	3.5	4	3.83	0.3726
22	189-2-8.	6	5.5	6	5.83	0.9901
23	190-3-8.	4.5	5	4.5	4.67	0.5373
24	191-4-8.	6	6	6	6.00	1.07
25	180-1-9.	1.5	1.5	1	1.33	0.0165
26	181-2-9.	2	2.5	2	2.17	0.0738
27	182-3-9.	1	1	1.5	1.17	0.0085
28	183-4-9.	2	2	2	2.00	0.05
29	204-1-10.	2	3	3	2.67	0.1438
30	205-2-10.	2	1	2	1.67	0.0335
31	1-1-11.	1	1	1	1.00	0
32	7-2-11.	1	1	1	1.00	0
33	9-3-11.	1	1	1	1.00	0
34	11-4-11.	1	1	1	1.00	0
35	2-1-12.	1	1	1	1.00	0
36	4-2-12.	1	1	1.5	1.17	0.0085
37	6-3-12.	1	2	1	1.33	0.0165
38	12-4-12.	1	1	1	1.00	0
39	3-1-13.	1.5	1	1.5	1.33	0.0165
40	5-2-13.	1	1	1	1.00	0
41	8-1-14.	1.5	1	1.5	1.33	0.0165
42	10-2-14.	1	1	1	1.00	0
43	37-1-15.	1	1	1	1.00	0
44	43-2-15.	1.5	1.5	1.5	1.50	0.025
45	45-3-15.	1	1.5	1	1.17	0.0085
46	47-4-15.	1	1	1	1.00	0
47	38-1-16.	1	1	1	1.00	0
48	40-2-16.	1	1	1	1.00	0
49	42-3-16.	1	1	1	1.00	0
50	48-4-16.	1	1	1	1.00	0
51	39-1-17.	1	1.5	1	1.17	0.0085
52	41-2-17.	1	1	1	1.00	0
53	44-1-18.	1.5	1	1	1.17	0.0085
54	46-2-18.	1	1	1.5	1.17	0.0085
55	73-1-19.	2	1.5	1	1.50	0.025
56	79-2-19.	1	1.5	1	1.17	0.0085
57	81-3-19.	1	1	1	1.00	0
58	83-4-19.	1	1.5	1	1.17	0.0085
59	74-1-20.	1	1	1	1.00	0
60	76-2-20.	1	1	1.5	1.17	0.0085
61	78-3-20.	1	1	1	1.00	0
62	84-4-20.	1	1	1	1.00	0
63	75-1-21.	1	1.5	1	1.17	0.0085
64	77-2-21.	1	1	1	1.00	0
65	80-1-22.	1	1.5	1	1.17	0.0085
66	82-2-22.	1	1	1	1.00	0
67	110-1-23.	1.5	1.5	1.5	1.50	0.025
68	112-2-23.	1	1	1	1.00	0
69	114-3-23.	1.5	1.5	1	1.33	0.0165
70	120-4-23.	1	2	1.5	1.50	0.025
71	10-1-24.	4	4	4	4.00	0.41
72	12-2-24.	2.5	2	2.5	2.33	0.0962
73	118-1-25.	3	3	3	3.00	0.19
74	120-2-25.	2.5	2	2	2.17	0.0738
75	79-1-26.	3.5	4	3.5	3.67	0.3374
76	81-2-26.	2.5	3	3	2.83	0.1662
77	83-3-26.	5	5	4.5	4.83	0.5677
78	84-4-26.	3.5	3	3	3.17	0.2274
79	159-1-27.	1.5	1.5	1.5	1.50	0.025
80	195-2-27.	2.5	3	3	2.83	0.1662
81	4-1-28.	3	3	3	3.00	0.19
82	12-2-28.	2.5	3	2.5	2.67	0.1438
83	157-1-29.	2	2	2	2.00	0.05
84	160-2-29.	1.5	2	1.5	1.67	0.0335
85	77-1-30.	1	1	1	1.00	0
86	84-2-30.	2	2	2	2.00	0.05
87	109-1-31.	1.5	1.5	1.5	1.50	0.025
88	115-2-31.	2	1.5	2	1.83	0.0415
89	117-3-31.	1.5	1	1	1.17	0.0085
90	120-4-31.	3	2.5	3	2.83	0.1662
91	38-1-32.	2	1.5	2	1.83	0.0415
92	40-2-32.	1.5	1	1.5	1.33	0.0165
93	46-3-32.	1	1.5	1.5	1.33	0.0165
94	48-4-32.	1.5	1.5	1.5	1.50	0.025
95	1-1-33.	2	2	2	2.00	0.05
96	2-2-33.	4	4	4	4.00	0.41
97	6-3-33.	2	2	2	2.00	0.05
98	12-4-33.	1.5	1.5	1.5	1.50	0.025
99	3-1-34.	3	2.5	3	2.83	0.1662
100	5-2-34.	1	1	1.5	1.17	0.0085
101	7-1-35.	5	5	5	5.00	0.6
102	9-2-35.	2.5	3	2.5	2.67	0.1438
103	8-1-36.	5	5	5	5.00	0.6
104	24-2-36.	4	4.5	4.5	4.33	0.4727
105	11-1-37.	1	1.5	1.5	1.33	0.0165
106	35-2-37.	1.5	1	1.5	1.33	0.0165
107	123-1-38.	1.5	1	1.5	1.33	0.0165
108	135-2-38.	2	3	2.5	2.50	0.12
109	143-3-38.	3	3	3	3.00	0.19
110	144-4-38.	4	3.5	3	3.50	0.3
111	37-1-39.	1	1	1	1.00	0
112	39-2-39.	1	1	1	1.00	0
113	41-3-39.	2	2	2	2.00	0.05
114	42-4-39.	3.5	3	3.5	3.33	0.2626
115	43-1-40.	2	2	2	2.00	0.05
116	44-2-40.	2	2	2	2.00	0.05
117	45-1-41.	2	2	2.5	2.17	0.0738
118	47-2-41.	3	2	2.5	2.50	0.12
119	74-1-42.	4	4	4.5	4.17	0.4423
120	76-2-42.	5	4.5	5	4.83	0.5677
121	78-3-42.	1	1.5	1	1.17	0.0085
122	84-4-42.	3	3	3	3.00	0.19
123	75-1-43.	1.5	1	1.5	1.33	0.0165

	SAMPLE	Porosity Observation				
	#	1	2	3	AVE.	%AREA
124	81-2-43.	1.5	1	1	1.17	0.0085
125	79-1-44.	3	3	3	3.00	0.19
126	80-2-44.	2	1.5	1.5	1.67	0.0335
127	82-1-45.	3	2.5	3	2.83	0.1662
128	94-2-45.	2.5	3	2.5	2.67	0.1438
129	83-1-46.	4	4.5	4	4.17	0.4423
130	95-2-46.	4	3.5	4	3.83	0.3726
131	110-1-47.	1	1	1.5	1.17	0.0085
132	112-2-47.	1	1	1	1.00	0
133	114-3-47.	3	2.5	3	2.83	0.1662
134	120-4-47.	2.5	2	2	2.17	0.0738
135	111-1-48.	1	1	1.5	1.17	0.0085
136	113-2-48.	1	1	1.5	1.17	0.0085
137	116-1-49.	1.5	1	1	1.17	0.0085
138	118-2-49.	1.5	2	1.5	1.67	0.0335
139	145-1-50.	2.5	3	3	2.83	0.1662
140	147-2-50.	3.5	4	3.5	3.67	0.3374
141	151-1-51.	2	1	1.5	1.50	0.025
142	155-2-51.	5	6	6	5.67	0.9149
143	158-1-52.	1.5	1	1	1.17	0.0085
144	160-2-52.	2.5	3	3	2.83	0.1662
145	164-1-53.	2	2	1.5	1.83	0.0415
146	168-2-53.	1	1	1	1.00	0
147	149-1-54.	1.5	1	1	1.17	0.0085
148	150-2-54.	1	1	1.5	1.17	0.0085
149	165-1-55.	3	3	2.5	2.83	0.1662
150	166-2-55.	1.5	1.5	1	1.33	0.0165
151	163-1-56.	1	1	1.5	1.17	0.0085
152	167-2-56.	1	1	1.5	1.17	0.0085
153	152-1-57.	1.5	1.5	1.5	1.50	0.025
154	156-2-57.	2.5	3	3	2.83	0.1662
155	13-1-58.	1	1	1	1.00	0
156	15-2-58.	1	1	1	1.00	0
157	17-3-58.	1	1	1	1.00	0
158	23-4-58.	2.5	3	2.5	2.67	0.1438
159	19-1-59.	3.5	3.5	3.5	3.50	0.3
160	21-2-59.	4	3.5	4	3.83	0.3726
161	26-1-60.	1.5	1.5	1	1.33	0.0165
162	28-2-60.	1	1	1	1.00	0
163	30-3-60.	1	1	1.5	1.17	0.0085
164	36-4-60.	2	2	1.5	1.83	0.0415
165	68-1-61.	3.5	3	3.5	3.33	0.2626
166	70-2-61.	1	1	1.5	1.17	0.0085
167	146-1-62.	1	1	1	1.00	0
168	148-2-62.	1	1	1.2	1.07	0.0035
169	153-1-63.	1	1	1	1.00	0
170	154-2-63.	1	1	1	1.00	0
171	161-1-64.	1.5	1	1	1.17	0.0085

	SAMPLE	Porosity Observation				
	#	1	2	3	AVE.	%AREA
172	162-2-64.	1	1	1	1.00	0
173	147-1-65.	1.5	1	1	1.17	0.0085
174	155-2-65.	1.5	1	1	1.17	0.0085
175	32-1-66.	3	3.5	3	3.17	0.2274
176	34-2-66.	3.5	4	3.5	3.67	0.3374
177	31-1-67.	4.5	4	4.5	4.33	0.4727
178	33-2-67.	4	4.5	4.5	4.33	0.4727
179	20-1-68.	3	3.5	3	3.17	0.2274
180	22-2-68.	1.5	1	1	1.17	0.0085
181	14-1-69.	2	3	2.5	2.50	0.12
182	18-2-69.	1.5	1.5	1.5	1.50	0.025
183	25-1-70.	1.5	1.5	1.5	1.50	0.025
184	27-2-70.	1	1	1	1.00	0
185	29-3-70.	1	1	1	1.00	0
186	35-4-70.	1	1	1.5	1.17	0.0085
187	49-1-72.	2	2	1.5	1.83	0.0415
188	51-2-72.	1.5	1	1.5	1.33	0.0165
189	53-3-72.	1.5	1	1.5	1.33	0.0165
190	59-4-72.	1	1.5	1	1.17	0.0085
191	55-1-73.	1.5	2	1.5	1.67	0.0335
192	57-2-73.	2	2	2	2.00	0.05
193	50-1-74.	1.5	1.5	1.5	1.50	0.025
194	52-2-74.	1	1.5	1.5	1.33	0.0165
195	54-3-74.	1	1	1.5	1.17	0.0085
196	60-4-74.	3	3	3	3.00	0.19
197	56-1-75.	1.5	1	1.5	1.33	0.0165
198	58-2-75.	1.5	2	1.5	1.67	0.0335
199	61-1-76.	2.5	3	3	2.83	0.1662
200	63-2-76.	1	1	1.5	1.17	0.0085
201	65-3-76.	1	1	1	1.00	0
202	71-4-76.	5	4.5	5.5	5.00	0.6
203	67-1-77.	1	1	1	1.00	0
204	69-2-77.	1	1	1	1.00	0
205	62-1-78.	1	1.5	1.5	1.33	0.0165
206	64-2-78.	1	1	1.5	1.17	0.0085
207	66-3-78.	1	1	1	1.00	0
208	72-4-78.	1.5	1.5	1.5	1.50	0.025
209	85-1-79.	1	1	1	1.00	0
210	87-2-79.	1.5	1.5	1	1.33	0.0165
211	89-3-79.	1	1	1	1.00	0
212	95-4-79.	1.5	1	1	1.17	0.0085
213	91-1-80.	1	1	1.5	1.17	0.0085
214	93-2-80.	1.5	1.5	1.5	1.50	0.025
215	86-1-81.	4.5	5	5	4.83	0.5677
216	88-2-81.	1	1	1.5	1.17	0.0085
217	90-3-81.	2	2.5	2.5	2.33	0.0962
218	96-4-81.	3	4	3.5	3.50	0.3
219	92-1-82.	1	1	1.5	1.17	0.0085

	SAMPLE	Porosity Observation				
	#	1	2	3	AVE.	%AREA
220	94-2-82.	2	1.5	1.5	1.67	0.0335
221	97-1-83.	3	3	3	3.00	0.19
222	99-2-83.	1	1	1	1.00	0
223	101-3-83.	1.5	1	1	1.17	0.0085
224	107-4-83.	5	4.5	4.5	4.67	0.5373
225	103-1-84.	3.5	3	3.5	3.33	0.0165
226	105-2-84.	1.5	1.5	1.5	1.50	0.025
227	98-1-85.	4.5	5	4	4.50	0.505
228	100-2-85.	1.5	1	1	1.17	0.0085
229	102-3-85.	2	2	1.5	1.83	0.0415
230	108-4-85.	5	5	5	5.00	0.6
231	104-1-86.	1	1.5	1	1.17	0.0085
232	106-2-86.	1.5	1	1	1.17	0.0085
233	121-1-87.	1	1	1	1.00	0
234	123-2-87.	1	1	1	1.00	0
235	125-3-87.	1	1	1	1.00	0
236	131-4-87.	1.5	1	1	1.17	0.0085
237	128-1-88.	4	4	3.5	3.83	0.3726
238	130-2-88.	1	1.5	1.5	1.33	0.0165
239	122-1-89.	1	1	1.5	1.17	0.0085
240	124-2-89.	1	1	1	1.00	0
241	126-3-89.	1.5	1	1	1.17	0.0085
242	132-4-89.	1.5	1	1.5	1.33	0.0165
243	127-1-90.	1.5	2	2	1.83	0.0415
244	129-2-90.	4	3.5	3.5	3.67	0.3374
245	133-1-91.	1	1	1	1.00	0
246	137-2-91.	1	1	1	1.00	0
247	139-1-92.	2	1.5	1.5	1.67	0.0335
248	141-2-92.	3.5	4	3.5	3.67	0.3374
249	140-1-93.	5	5	4.5	4.83	0.5677
250	142-2-93.	2.5	3	2.5	2.67	0.1438
251	131-1-94.	1	1	1	1.00	0
252	136-2-94.	1	1	1	1.00	0
253	138-3-94.	1.5	1	1	1.17	0.0085
254	144-4-94.	1.5	1	1	1.17	0.0085
255	169-1-95.	1	1	1	1.00	0
256	170-2-95.	1	1	1	1.00	0
257	171-1-96.	1.5	1.5	1.5	1.50	0.025
258	172-2-96.	1	1	1.5	1.17	0.0085
259	200-1-97.	1	1	1	1.00	0
260	201-2-97.	1.5	2	2	1.83	0.0415
261	199-1-98.	1.5	1	1	1.17	0.0085
262	203-2-98.	1.5	1	1	1.17	0.0085
263	177-1-99.	1	1	1	1.00	0
264	178-2-99.	1	1	1	1.00	0
265	179-1-100	1	1.5	1.5	1.33	0.0165
266	181-2-100	1	1	1	1.00	0
267	197-1-101	3	2.5	3	2.83	0.1662

	SAMPLE	Porosity Observation				
	#	1	2	3	AVE.	%AREA
268	198-2-101.	5	4.5	4.5	4.67	0.5373
269	185-1-102.	2	2	2	2.00	0.05
270	186-2-102.	1.5	1	1	1.17	0.0085
271	14-1-103.	1	1	1	1.00	0
272	18-2-103.	2	2	2	2.00	0.05
273	16-1-104.	2	2	2	2.00	0.05
274	22-2-104.	4.5	4	4.5	4.33	0.4727
275	57-1-105.	1.5	1	1	1.17	0.0085
276	58-2-105.	2.5	3	2.5	2.67	0.1438
277	52-1-106.	1.5	1	1	1.17	0.0085
278	70-2-106.	1	1	1	1.00	0
279	25-1-107.	2	2	1.5	1.83	0.0415
280	31-2-107.	1	1	1.5	1.17	0.0085
281	50-1-108.	1	1	1	1.00	0
282	58-2-108.	3	2.5	3	2.83	0.1662
283	57-1-109.	2	2	2	2.00	0.05
284	71-2-109.	1	1	1.5	1.17	0.0085
285	91-1-110.	2	2.5	3	2.50	0.12
286	93-2-110.	1.5	1.5	2	1.67	0.0335
287	173-1-111.	1	1	1	1.00	0
288	174-2-111.	1	1.5	1.5	1.33	0.0165
289	182-1-112.	2.5	3	2.5	2.67	0.1438
290	183-2-112.	1	1	1	1.00	0
291	185-1-113.	2	2	1.5	1.83	0.0415
292	186-2-113.	1	1	1.5	1.17	0.0085
293	175-1-114.	2.5	2	2	2.17	0.0738
294	176-2-114.	4.5	4	4.5	4.33	0.4727
295	180-1-115.	3.5	3	3.5	3.33	0.2626
296	182-2-115.	4	4.5	4	4.17	0.4423
297	189-1-116.	5	5	5	5.00	0.6
298	190-2-116.	5.5	5	5	5.17	0.6799
299	192-1-117.	2	2	2	2.00	0.05
300	193-2-117.	3	3	3	3.00	0.19
301	194-1-118.	5	5	5	5.00	0.6
302	195-2-118.	4.5	5	4.5	4.67	0.5373
303	197-1-119.	4.5	5	4.5	4.67	0.5373
304	198-2-119.	5.5	6	5.5	5.67	0.9149
305	154-1-120.	2	1.5	1.5	1.67	0.0335
306	191-2-120.	6	6	6	6.00	1.07
307	92-1-121.	5	5	4.5	4.83	0.5677
308	108-2-121.	1	1	1.5	1.17	0.0085
309	103-1-122.	2	1.5	2	1.83	0.0415
310	107-2-122.	1.5	1.5	1.5	1.50	0.025
311	173-1-123.	2	2	2	2.00	0.05
312	174-2-123.	5	4.5	5	4.83	0.5677
313	41-1-124.	6	6	6	6.00	1.07
314	60-2-124.	6	6	6	6.00	1.07
315	195-1-125.	4	4	4	4.00	0.41

	SAMPLE	Porosity Observation				
	#	1	2	3	AVE.	%AREA
316	198-2-125	5	5	6	5.33	0.7551
317	184-1-126	1	1	1	1.00	0
318	189-2-126	1.5	1	1	1.17	0.0085
319	182-1-127	1	1	1	1.00	0
320	183-2-127	1.5	2	2	1.83	0.0415
321	180-1-128	1	1	1	1.00	0
322	164-2-128	3	3	3	3.00	0.19
323	173-1-129	1	1	1	1.00	0
324	146-2-129	1	1	1	1.00	0
325	41-1-130.	1	1	1	1.00	0
326	60-2-130.	3	3.5	3.5	3.33	0.2626
327	81-1-131.	1.5	1.5	1.5	1.50	0.025
328	288-2-131	1.5	1.5	1.5	1.50	0.025
329	120-1-132	1.5	1	1	1.17	0.0085
330	289-2-132	2	2	2	2.00	0.05
331	173-1-133	4.5	4.5	4.5	4.50	0.505
332	153-2-133	4	4	4	4.00	0.41
333	41-1-134.	4	4	4	4.00	0.41
334	60-2-134.	4.5	5	5	4.83	0.5677
335	173-1-135	5	5	5.5	5.17	0.6799
336	212-2-135	5	5	5	5.00	0.6
337	224-1-136	2	1.5	2	1.83	0.0415
338	227-2-136	5	5	5.5	5.17	0.6799
339	252-1-137	3	3	3	3.00	0.19
340	289-2-137	1.5	1.5	1.5	1.50	0.025
341	261-1-138	1	1	1.5	1.17	0.0085
342	264-2-138	3.5	3	3.5	3.33	0.2626
343	218-1-139	2	2	1.5	1.83	0.0415
344	233-2-139	2	2	1.5	1.83	0.0415
345	238-1-140	4	4	4	4.00	0.41
346	240-2-140	3.5	3.5	3.5	3.50	0.3
347	255-1-141	2	2	2	2.00	0.05
348	258-2-141	3	3	3	3.00	0.19
349	274-1-142	2	2	2	2.00	0.05
350	278-2-142	4	4	4	4.00	0.41
351	275-1-143	1.5	2	1.5	1.67	0.0335
352	279-2-143	2.5	3	2	2.50	0.12
353	276-1-144	1.5	2	1.5	1.67	0.0335
354	280-2-144	2	2	2	2.00	0.05
355	236-1-146	1	1.5	1.5	1.33	0.0165
356	264-2-146	2	1.5	1.5	1.67	0.0335
357	28-1-148.	4.5	4	4.5	4.33	0.4727
358	60-1-149.	5	5	5	5.00	0.6
359	32-1-150.	4	4	4	4.00	0.41
360	134-1-151	1	1	1	1.00	0
361	215-1-152	2	2.5	2	2.17	0.0738
362	221-2-152	1	1	1	1.00	0
363	230-1-153	2	2	2	2.00	0.05

	SAMPLE	Porosity Observation				
	#	1	2	3	AVE.	%AREA
364	233-2-153	1.5	1	1.5	1.33	0.0165
365	206-1-154	6	6	6	6.00	1.07
366	258-2-154	2	1.5	1.5	1.67	0.0335
367	240-1-154	2.5	2.5	2.5	2.50	0.12
368	209-1-155	4	3.5	4	3.83	0.3726
369	274-1-155	3	2.5	3.5	3.00	0.19
370	278-2-155	4.5	4.5	4	4.33	0.4727
371	275-1-156	1.5	1.5	1.5	1.50	0.025
372	221-1-156	3.5	3	3	3.17	0.2274
373	279-2-156	5	4.5	5	4.83	0.5677
374	233-1-157	2	1.5	2	1.83	0.0415
375	258-1-158	4	4.5	4	4.17	0.4423
376	264-1-159	6	6	6	6.00	1.07
377	275-1-160	5.5	6	5.5	5.67	0.9149
378	279-1-161	6	6	6	6.00	1.07
379	292-1-162	6	6	6	6.00	1.07
380	289-1-163	6	5	5	5.33	0.7551
381	293-1-164	5	5	5	5.00	0.6
382	278-1-165	7	6.5	7	6.83	1.4352
383	291-1-166	6	6	6	6.00	1.07
384	283-1-167	5	5.5	5	5.17	0.6799
385	169-1-168	4	4	4	4.00	0.41
386	233-1-169	3	3	3	3.00	0.19
387	258-1-170	3.5	3	4	3.50	0.3
388	277-1-171	4	5	4	4.33	0.4727
389	269-1-172	5	5	5	5.00	0.6
390	269-1-173	3.5	3.5	4	3.67	0.3374
391	282-1-174	1	1.5	1.5	1.33	0.0165
392	205-1-175	3	3.5	4	3.50	0.3
393	278-1-176	5	5	5	5.00	0.6
394	169-1-177	5	4.5	5	4.83	0.5677
395	207-1-178	1	1	1	1.00	0
396	208-1-179	6	6	6	6.00	1.07
397	211-1-180	1	1	1.5	1.17	0.0085
398	214-1-181	1	1.5	2	1.50	0.025
399	217-1-182	3	3	3	3.00	0.19
400	220-1-183	2	1.5	2	1.83	0.0415
401	225-1-184	2	2.5	1.5	2.00	0.05
402	207-1-185	1.5	1.5	1.5	1.50	0.025
403	211-1-186	1.5	1	1	1.17	0.0085
404	214-1-187	6	6	6	6.00	1.07
405	233-1-188	5.5	6	5.5	5.67	0.9149
406	226-1-189	3.5	4	4	3.83	0.3726
407	229-1-190	1.5	1.5	1.5	1.50	0.025
408	232-1-191	4	3.5	3.5	3.67	0.3374
409	235-1-192	1	1	1	1.00	0
410	239-1-193	1.5	1.5	1.5	1.50	0.025
411	251-1-194	1.5	1.5	1.5	1.50	0.025

	SAMPLE	Porosity Observation				
	#	1	2	3	AVE.	%AREA
412	254-1-195.	4.5	4	4	4.17	0.4423
413	257-1-196.	1.5	1.5	1	1.33	0.0165
414	263-1-197.	1	1	1	1.00	0
415	267-1-198.	6	6	6	6.00	1.07
416	273-1-199.	1.5	1.5	1.5	1.50	0.025
417	260-1-200.	1	1	1.5	1.17	0.0085
418	233-1-201.	6	6	6	6.00	1.07
419	213-1-202.	1.5	1	1	1.17	0.0085
420	216-1-203.	1	1	1.5	1.17	0.0085
421	285-1-204.	1	1.5	1.5	1.33	0.0165
422	270-1-205.	1.5	1	1	1.17	0.0085
423	271-1-206.	5	5	5	5.00	0.6
424	207-1-207.	6	6	6	6.00	1.07
425	210-1-208.	1.5	1	1	1.17	0.0085
426	233-1-209.	1	1	1	1.00	0
427	239-1-210.	3.5	4	3	3.50	0.3
428	251-1-211.	1	1	1	1.00	0
429	260-1-212.	1.5	1.5	1	1.33	0.0165
430	267-1-213.	1.5	1	1	1.17	0.0085
431	269-1-214.	1.5	1.5	1.5	1.50	0.025
432	275-1-215.	1	1	1	1.00	0
433	289-1-216.	1	1	1	1.00	0
434	207-1-217.	1.5	1	1	1.17	0.0085
435	210-1-218.	3	3.5	2.5	3.00	0.19
436	272-1-219.	4.5	5	4.5	4.67	0.5373
437	240-1-220.	3.5	3	3	3.17	0.2274
438	258-1-221.	6	6	6	6.00	1.07
439	213-1-222.	5.5	6	5.5	5.67	0.9149

	SAMPLE	Porosity Observation				
	#	1	2	3	AVE.	%AREA
440	219-1-223	1.5	1	1	1.17	0.0085
441	222-1-224	2	2	2	2.00	0.05
442	225-1-225	5.5	6	6	5.83	0.9901
443	228-1-226	3	2.5	3.5	3.00	0.19
444	233-1-227	5	6	5	5.33	0.7551
445	234-1-228	2	1.5	1.5	1.67	0.0335
446	231-1-229	4	4.5	5	4.50	0.505
447	237-1-230	2	2	2	2.00	0.05
448	240-1-231	3.5	4	4	3.83	0.3726
449	250-1-232	3	3	3.5	3.17	0.2274
450	251-1-233	5.5	4.5	5	5.00	0.6
451	253-1-234	5.5	6	5.5	5.67	0.9149
452	256-1-235	3	3.5	3	3.17	0.2274
453	289-1-236	5.5	5	6	5.50	0.835
454	259-1-237	5	5	5	5.00	0.6
455	260-1-238	2.5	3	2	2.50	0.12
456	281-1-239	6	6	6	6.00	1.07
457	262-1-240	4	3.5	4	3.83	0.3726
458	265-1-241	6	5.5	5	5.50	0.835
459	277-1-242	2.5	2	3	2.50	0.12
460	275-1-243	1	1.5	1	1.17	0.0085
461	276-1-244	3	3	3	3.00	0.19
462	279-1-245	4.5	5	6	5.17	0.6799
463	280-1-246	4.5	5	4.5	4.67	0.5373
464	282-1-247	4.5	4	4.5	4.33	0.4727
465	284-1-248	5	4.5	5	4.83	0.5677
466	283-1-249	4	4	3.5	3.83	0.3726
467	286-1-250	4.5	4	4	4.17	0.4423

	SAMPLE	Porosity Observation				
	#	1	2	3	AVE.	%AREA
468	287-1-251	2	1.5	1.5	1.67	0.0335
469	293-1-252	4.5	5	5.5	5.00	0.6
470	291-1-253	1	1.5	1	1.17	0.0085
471	292-1-254	6	5.5	5	5.50	0.835
472	234-1-255	6	5	5.5	5.50	0.835
473	237-1-256	5.5	6	5.5	5.67	0.9149
474	251-1-257	4.5	4.5	4.5	4.50	0.505
475	256-1-258	1.5	1.5	2	1.67	0.0335
476	259-1-259	4.5	5	5	4.83	0.5677
477	260-1-260	1.5	2	1.5	1.67	0.0335
478	281-1-261	5	5.5	6	5.50	0.835
479	234-1-262	1	1	1	1.00	0
480	251-1-263	3.5	4	3.5	3.67	0.3374
481	256-1-264	1	1	1	1.00	0
482	259-1-265	3	3.5	3.5	3.33	0.2626
483	275-1-266	1	1	1	1.00	0
484	276-1-267	1	1	1	1.00	0
485	279-1-268	3.5	4.5	4	4.00	0.41
486	294-1-269	1	1	1	1.00	0
487	RM10	4	4.5	4.5	4.33	0.4727
488	RM11	5	6	6	5.67	0.9149
489	HAM1	1	1	1	1.00	0
490	AX65	1	1	1	1.00	0
491	RMF	1	1	1	1.00	0
492	RMG	2	1.5	1.5	1.67	0.0335
493	RMX	5	5	5	5.00	0.6
494	RMY	1.5	1.5	1	1.33	0.0165
495	RMZ	1	1	1	1.00	0

Appendix K

Vickers Hardness Test Results.

	Sample	Hv10 test data.							
	#	1	2	3	4	5	6	AVE	STD. DEV.
1	37-1-2.	42.6	42.1	43.6	42.6	42.1	43.9	42.8	0.7627
2	43-2-2.	52.6	50.7	49.8	50	50.3	49.5	50.5	1.1161
3	44-3-2.	52.9	52.2	52.6	52	52.7	54	52.7	0.7033
4	48-4-2.	54.9	54.7	53.1	52.2	54.4	54.2	53.9	1.0496
5	61-1-3.	41.6	41.6	40.5	40.8	40.7	40.6	41	0.5007
6	67-2-3.	50.8	51.5	50.5	50	50.2	51.2	50.7	0.5797
7	68-3-3.	51.5	49.3	49.3	48.9	50.3	49.3	49.8	0.9688
8	72-4-3.	54	50	50.5	52.9	48.1	51.2	51.1	2.1085
9	1-1-4.	45	45.7	45	45.6	45	45.3	45.3	0.3204
10	7-2-4.	48.1	46.9	45.3	46.9	47.3	46.4	46.8	0.9347
11	8-3-4.	48.7	48.7	48.4	47.3	47.6	49.3	48.3	0.7501
12	12-4-4.	48.6	48.1	51.9	54	49.8	49.8	50.4	2.2115
13	109-1-5.	48.2	48.9	48.1	45.6	49	47.5	47.9	1.2481
14	120-2-5.	53.8	57.7	54.9	53.6	53.1	55.1	54.7	1.6601
15	97-1-6.	48.1	48.7	47.9	47.2	46.3	47.8	47.7	0.8262
16	108-2-6.	57.3	53.8	55.1	62	56.3	54.9	56.6	2.9228
17	169-1-7.	45.8	46.1	47.2	45.6	45.6	45.6	46	0.6274
18	170-2-7.	45.7	46.9	45.4	48.6	46.3	48.2	46.9	1.3126
19	171-3-7.	48.5	48.5	48	48.8	49	46.7	48.3	0.8313
20	172-4-7.	47	46.4	46.4	46.4	46.4	46.9	46.6	0.2858
21	188-1-8.	50.3	54.7	55.1	54.4	54.6	53.1	53.7	1.7989
22	189-2-8.	57.9	57.5	53.6	53.6	52.2	54.6	54.9	2.303
23	190-3-8.	54	55.1	55.5	55.1	55.9	52.7	54.7	1.1737
24	191-4-8.	51.5	52.9	52.9	52.6	54	53.3	52.9	0.8262
25	180-1-9.	41.8	53.5	42.8	42.8	43.9	43.2	44.7	4.3807
26	181-2-9.	46.9	46.1	45.3	44.7	44.4	44.6	45.3	0.9852
27	182-3-9.	46.1	46.4	43.2	46.1	47.2	46.3	45.9	1.3761
28	183-4-9.	45.8	43.9	46.6	45.8	44.9	43.9	45.2	1.1077
29	204-1-10	48.2	49.2	48.1	48.2	47.9	50.5	48.7	0.9988
30	205-2-10	50.5	52.7	48.6	48.7	50.3	49.7	50.1	1.5052
31	1-1-11.	50.3	49.8	48.6	49.8	51	45.6	49.2	1.9229
32	7-2-11.	49.8	49.8	50.3	48.6	47.6	45.1	48.5	1.949
33	9-3-11.	48.6	47	50.5	47.9	48.6	50.3	48.8	1.3615
34	11-4-11.	50.2	50.5	49.5	49.2	49.2	49	49.6	0.6099
35	2-1-12.	48.2	54.4	55.1	54.2	54.2	49.3	52.6	2.9951
36	4-2-12.	49	48.7	48.9	48.9	46.9	48.9	48.6	0.8142
37	6-3-12.	55.3	56.1	53.8	52	53.8	52.6	53.9	1.5565
38	12-4-12.	53.3	54.7	52	54.2	52.4	53.6	53.4	1.0328
39	3-1-13.	51.5	49.7	46.6	48.7	48.4	48.9	49	1.6096
40	5-2-13.	51.2	50.8	48.7	47.2	49.8	49.8	49.6	1.4593
41	8-1-14.	47.5	48.2	49.3	50.3	49.5	48.7	48.9	0.9968
42	10-2-14.	49.8	52	50.2	50.5	50.2	50.5	50.5	0.7633

	Sample	Hv10 test data.							
	#	1	2	3	4	5	6	AVE	STD. DEV.
43	37-1-15.	46.3	46.9	45.3	45.8	46.4	47.6	46.4	0.8085
44	43-2-15.	47.5	48.4	47.6	47	47.6	49.7	48	0.9606
45	45-3-15.	51.2	53.3	50.2	53.8	50.3	48.7	51.3	1.9604
46	47-4-15.	49.3	49.3	49.3	53.6	50.2	50	50.3	1.6726
47	38-1-16.	51.2	48.2	48.4	47.9	47.3	49.3	48.7	1.3819
48	40-2-16.	51.2	51.5	50.7	51.5	48.9	50.2	50.7	1.0013
49	42-3-16.	55.1	55.1	52	52.7	55.1	52	53.7	1.5908
50	48-4-16.	55.1	54.9	50.3	54.9	50.3	55.3	53.5	2.4574
51	39-1-17.	45.3	45	45.8	46	44.3	44.3	45.1	0.725
52	41-2-17.	50.2	50.2	50.2	50.7	51.3	50.7	50.6	0.4416
53	44-1-18.	50.7	49.2	48.9	49.7	50	51.2	50	0.8781
54	46-2-18.	49.7	48.6	48.6	48.1	51.7	52	49.8	1.6869
55	73-1-19.	48.6	52.2	49	50.2	51	49	50	1.4029
56	79-2-19.	51.5	49.3	50.7	52.2	51.7	52.5	51.3	1.1669
57	81-3-19.	50	48.1	50.2	48.9	49.3	51	49.6	1.0304
58	83-4-19.	56.3	52.4	55.1	55.3	54.7	50.7	54.1	2.1018
59	74-1-20.	55.9	53.8	55.9	55.9	55.1	56.9	55.6	1.0439
60	76-2-20.	56.3	54	51.3	52.2	52.9	52	53.1	1.8082
61	78-3-20.	53.1	54.6	56.1	56.5	55.3	58.3	55.7	1.7706
62	84-4-20.	53.6	56.1	54.4	56.1	56.1	57.7	55.7	1.4542
63	75-1-21.	49.5	53.3	51.3	52	52.6	49.5	51.4	1.5895
64	77-2-21.	51.5	52	51.5	49.8	52	52.9	51.6	1.0265
65	80-1-22.	52.4	53.3	55.9	46	51.9	50.8	51.7	3.2872
66	82-2-22.	54	55.5	55.5	55.5	55.1	53.3	54.8	0.9432
67	110-1-23	49.2	56.7	56.1	56.1	49.2	51.5	53.1	3.5758
68	112-2-23	52.6	56.7	52	56.3	55.7	52.4	54.3	2.1683
69	114-3-23	54.7	52.9	53.6	53.6	53.3	56.9	54.2	1.4665
70	120-4-23	52.6	54.4	60.4	61.3	55.5	53.8	56.3	3.633
71	10-1-24.	52.4	52.6	55.3	58.5	55.7	54.6	54.9	2.2528
72	12-2-24.	58.1	53.1	51.3	53.3	52.7	54.7	53.9	2.3441
73	118-1-25	46.4	54.6	53.3	53.6	53.3	54.4	52.6	3.0874
74	120-2-25	50.7	54	52	51.2	51.9	52.6	52.1	1.1553
75	79-1-26.	53.3	53.8	53.5	52.7	51	55.3	53.3	1.4095
76	81-2-26.	46.6	53.8	53.1	53.1	53.1	57.1	52.8	3.4117
77	83-3-26.	52.6	52.2	54.9	57.9	58.1	50.7	54.4	3.0971
78	84-4-26.	55.7	55.7	59.8	59.3	57.1	55.7	57.2	1.4665
79	159-1-27	47.5	48.7	50.2	49	49.8	49.2	49.1	0.9416
80	195-2-27	53.6	49.8	49.8	53.3	52.7	52.7	52	1.7268
81	4-1-28.	48.9	50.3	50.7	50.2	50.5	50	50.1	0.6356
82	12-2-28.	51.7	51	50.5	51.7	49.8	50.5	50.9	0.7501
83	157-1-29	48.2	47.8	48.6	47.9	48.9	47.8	48.2	0.4604
84	160-2-29	50.3	48.9	49.2	51	48.6	50	49.7	0.9201

	Sample	Hv10 test data.							
	#	1	2	3	4	5	6	AVE	STD. DEV.
85	77-1-30.	51.5	51.9	51.5	53.1	52	51.7	52	0.5992
86	84-2-30.	52.2	55.5	55.3	54.2	57.1	59.1	55.6	2.3712
87	109-1-31	47.3	54.6	47.5	49.5	49.8	49	49.6	2.6498
88	115-2-31	50.3	52	52.4	54.2	48.9	48.4	51	2.2295
89	117-3-31	49.5	52.6	55.1	54.7	52.2	52.2	52.7	2.0253
90	120-4-31	51.5	59.8	56.1	55.7	56.3	53.1	55.4	2.8722
91	38-1-32.	47.3	46.7	45.3	43.9	46	47	46	1.2707
92	40-2-32.	44	48.2	48.1	49.5	50.2	47.5	47.9	2.1609
93	46-3-32.	54.9	54	54	52.6	54.2	55.3	54.2	0.9309
94	48-4-32.	51.3	52.7	51	52.6	54.6	54	52.7	1.4255
95	1-1-33.	47.6	46	46.7	45.7	46.7	45.1	46.3	0.8832
96	2-2-33.	48.4	48.4	49	49.7	49	48.1	48.8	0.582
97	6-3-33.	48.6	49.8	50.5	50.3	51.5	50.2	50.2	0.9482
98	12-4-33.	52.7	51.7	50.2	54.4	50.2	52.7	52	1.6315
99	3-1-34.	45.1	46.7	47.5	47.5	46.9	46.9	46.8	0.8824
100	5-2-34.	46	46.9	46.9	47.6	47.3	48.9	47.3	0.9647
101	7-1-35.	47.9	46.9	48.6	49.7	47.9	49.4	48.4	1.0469
102	9-2-35.	53.4	51	51	49.8	50.3	51.3	51.1	1.2388
103	8-1-36.	49.8	48.1	50.7	50.8	52.2	50.7	50.4	1.3586
104	24-2-36.	52.2	57.5	52.4	55.9	55.7	56.3	55	2.1836
105	11-1-37.	51	52	52.7	52.4	53.4	52	52.3	0.8044
106	35-2-37.	55.7	56.9	58.3	59.8	57.9	48.3	56.2	4.084
107	123-1-38	47.5	49.8	56.1	51.5	51	47.5	50.6	3.196
108	135-2-38	48.1	48.1	50.2	52.4	51	50.8	50.1	1.7088
109	143-3-38	57.3	57.3	57.3	58.3	56.7	56.7	57.3	0.5854
110	144-4-38	56.3	57.9	62.2	60.9	62.2	57.9	59.6	2.5248
111	37-1-39.	41.1	42.2	42.3	42.8	43.2	44.8	42.7	1.2356
112	39-2-39.	45.8	46.1	45.7	45.1	45.3	44.7	45.5	0.5128
113	41-3-39.	47.9	45.8	48.4	47.9	46.4	45.4	47	1.2596
114	42-4-39.	48.7	49.4	46.7	46.3	49.7	48	48.1	1.401
115	43-1-40.	48.6	49.8	49.8	48.9	49	49.7	49.3	0.5292
116	44-2-40.	51	51.5	50.8	51.5	48.9	52.2	51	1.1303
117	45-1-41.	48.2	48.2	50.2	50	51	49.2	49.5	1.1361
118	47-2-41.	51.5	54.6	55.1	53.1	53.1	51.5	53.2	1.507
119	74-1-42.	50.7	53.8	53.3	56.7	55.1	55.3	54.2	2.0724
120	76-2-42.	55.1	57.9	55.5	55.1	56.5	56.3	56.1	1.0764
121	78-3-42.	54.2	52.4	51.3	54.2	52.4	51	52.6	1.3747
122	84-4-42.	56.3	59.3	58.1	60.4	58.9	59.3	58.7	1.3977
123	75-1-43.	51.9	52	52.2	55.5	54.6	52.6	53.1	1.5306
124	81-2-43.	52.4	54	53.3	53.8	55.3	54.7	53.9	1.0226
125	79-1-44.	52.9	51.3	50.2	51.9	51.9	51.3	51.6	0.8954
126	80-2-44.	53.4	59.1	57.3	53.6	57.7	55.3	56.1	2.3312
127	82-1-45.	55.1	58.3	57.1	55.5	58.3	60.2	57.4	1.9209
128	94-2-45.	57.1	61.3	56.3	57.1	60.2	56.1	58	2.184
129	83-1-46.	52.9	54.4	55.9	54	52	53.6	53.8	1.3342
130	95-2-46.	51.5	54.7	52.7	55.1	54	52.2	53.4	1.4473
131	110-1-47	48.6	51.9	52	53.4	54	51.5	51.9	1.8826
132	112-2-47	52	54.2	55.5	54.6	52.9	50.7	53.3	1.786
133	114-3-47	49	49.7	50.8	49.8	50.7	49.7	50	0.6834

	Sample	Hv10 test data.							
	#	1	2	3	4	5	6	AVE	STD. DEV.
134	120-4-47	54.4	55.7	54.9	57.1	54.9	52.7	55	1.4529
135	111-1-48	46	50.7	50.5	50.2	48.2	48.1	49	1.8447
136	113-2-48	49	53.8	51	54.4	53.8	49.8	52	2.3269
137	116-1-49	52	54.4	57.1	54.4	50.7	46.7	52.6	3.6193
138	118-2-49	53.6	61.3	53.1	56.1	57.5	55.1	56.1	3.0083
139	145-1-50	47.5	49.7	45.3	48.7	50.3	45	47.8	2.2287
140	147-2-50	49.2	51.5	51.5	49	52.7	47.8	50.3	1.8862
141	151-1-51	50.3	52.2	52.6	53.1	51.2	52.4	52	1.0289
142	155-2-51	53.6	51.5	54.6	52.4	52.9	53.2	53	1.0558
143	158-1-52	50.2	51.5	50.2	50.2	53.4	51	51.1	1.2561
144	160-2-52	49.7	56.9	54.4	55.5	51.9	49.7	53	3.0466
145	164-1-53	53.6	49.5	53.6	54.6	54.7	52.6	53.1	1.9246
146	168-2-53	57.5	59.1	57.1	56.1	53.3	46.7	55	4.4823
147	149-1-54	49.7	52.2	53.4	53.1	52.4	54	52.5	1.5069
148	150-2-54	48.6	57.5	54.7	54.9	54.9	54.4	54.2	2.95
149	165-1-55	50.2	49.5	50.8	50.5	46.3	49.7	49.5	1.6407
150	166-2-55	51.5	51.2	51.3	53.3	53.1	51.2	51.9	0.9893
151	163-1-56	54	57.1	56.9	53.8	55.3	51.3	54.7	2.1824
152	167-2-56	54.2	52	55.5	54.7	56.3	52	54.1	1.7882
153	152-1-57	57.9	58.9	59.1	57.9	57.9	57.9	58.3	0.5715
154	156-2-57	60.2	62	61.7	59.1	60.9	63.1	61.2	1.4137
155	13-1-58.	47.6	47.6	46.9	47.3	46.7	47.3	47.2	0.367
156	15-2-58.	49.5	49.2	50.3	49.5	49.4	49.8	49.6	0.3869
157	17-3-58.	50.3	51.3	51.7	51.2	51.5	50.7	51.1	0.5231
158	23-4-58.	56.1	45.3	58.1	56.7	53.1	48.6	53	5.059
159	19-1-59.	51	51.9	52.2	51.2	52.7	50.8	51.6	0.7501
160	21-2-59.	52.2	54	53.4	54.2	53.4	52.6	53.3	0.7772
161	26-1-60.	49.4	51.9	50.5	51	51.5	49	50.6	1.1537
162	28-2-60.	55.5	54.7	54.7	53.6	53.4	52.6	54.1	1.0647
163	30-3-60.	50.8	52.9	53.8	53.3	54	53.3	53	1.1548
164	36-4-60.	59.1	52.7	59.3	58.9	59.8	60.6	58.4	2.858
165	68-1-61.	51	51.8	53.3	52.9	55.1	56.7	53.5	2.1134
166	70-2-61.	57.7	57.3	57.3	57.7	57.3	59.1	57.7	0.6976
167	146-1-62	52.9	54	56.3	57.1	53.3	54.7	54.7	1.6738
168	148-2-62	53.4	55.1	56.1	57.5	57.5	54.2	55.6	1.7037
169	153-1-63	47.6	49.5	48.9	49.2	50.5	49.7	49.2	0.9668
170	154-2-63	50.2	51.9	51.2	51.3	50	48.6	50.5	1.186
171	161-1-64	48.6	47.5	46.6	47.2	47.5	47.3	47.5	0.6535
172	162-2-64	52.4	52	54	51.7	52.7	53.4	52.7	0.8672
173	147-1-65	51.2	54.4	53.6	53.8	53.4	53.8	53.4	1.113
174	155-2-65	57.5	55.1	56.1	55.9	57.3	58.5	56.7	1.2485
175	32-1-66.	56.7	57.7	57.3	58.7	57.1	55.5	57.2	1.0633
176	34-2-66.	59.1	58.7	59.6	58.3	58.1	58.3	58.7	0.5742
177	31-1-67.	52.7	53.6	53.6	54.2	53.6	52.4	53.4	0.6686
178	33-2-67.	53.6	53.3	54.9	56.7	53.6	53.4	54.3	1.3338
179	20-1-68.	54	55.7	57.5	56.9	56.1	54.2	55.7	1.4123
180	22-2-68.	58.9	53.4	58.1	58.9	56.9	59.6	57.6	2.2695
181	14-1-69.	48.9	49.8	52.2	50.8	51.5	50.8	50.7	1.1793
182	18-2-69.	50.2	49.5	51.2	51	49.8	50.5	50.4	0.6653

	Sample	Hv10 test data.							
	#	1	2	3	4	5	6	AVE	STD. DEV.
183	25-1-70.	46.9	47.3	46.7	45.6	47	46.6	46.7	0.5845
184	27-2-70.	48.6	47.9	49	48.9	48.7	48.6	48.6	0.3869
185	29-3-70.	51.3	51.2	51.2	50.3	51.5	54.6	51.7	1.4878
186	35-4-70.	54.6	55.1	57.1	58.9	57.9	55.1	56.5	1.7661
187	49-1-72.	44.7	45	45	44.6	45	45	44.9	0.1835
188	51-2-72.	47.2	46.7	46	46	46.9	47	46.6	0.5164
189	53-3-72.	47	47.3	47	47	47	48.1	47.2	0.4412
190	59-4-72.	59.6	53.3	54.2	54.9	55.1	53.6	55.1	2.306
191	55-1-73.	45.8	50	49.5	50.7	49.8	50.8	49.4	1.8511
192	57-2-73.	54	53.6	53.5	51.5	49.7	56.5	53.1	2.3192
193	50-1-74.	47.2	47	47.3	46.6	47.2	46.7	47	0.2898
194	52-2-74.	49.5	48.7	48.2	48.2	49.4	48.9	48.8	0.5636
195	54-3-74.	47.2	47.8	48.4	48.2	49.7	50.7	48.7	1.2956
196	60-4-74.	56.9	55.9	55.1	57.5	55.5	55.5	56.1	0.9331
197	56-1-75.	55.1	53.8	53.8	53.1	52.9	53.8	53.8	0.7714
198	58-2-75.	54.9	57.3	56.5	57.1	55.1	55.5	56.1	1.0386
199	61-1-76.	45.3	45.8	45	46.9	45.3	45.7	45.7	0.6713
200	63-2-76.	47.5	46.3	46.7	46.3	46.7	48.4	47	0.8208
201	65-3-76.	48.9	48.4	48.9	50.2	49.2	49.5	49.2	0.6178
202	71-4-76.	52.6	55.7	55.9	56.1	58.7	54.2	55.5	2.0442
203	67-1-77.	58.5	55.1	54.7	54.9	56.1	55.9	55.9	1.4052
204	69-2-77.	52.2	51.7	51.3	52.4	51.7	53.8	52.2	0.8841
205	62-1-78.	49.8	48.1	49.8	46.7	48.6	49.7	48.8	1.2449
206	64-2-78.	55.7	54	52.6	52.7	52.2	56.1	53.9	1.6798
207	66-3-78.	53.3	52.4	51.5	48.2	49.7	48.1	50.5	2.197
208	72-4-78.	56.3	52.6	56.3	54.4	58.3	57.1	55.8	2.0314
209	85-1-79.	55.7	55.9	53.8	54.9	54	56.5	55.1	1.0857
210	87-2-79.	54.4	53.6	52.6	53.8	54	51.7	53.4	1.0075
211	89-3-79.	46	55.1	56.5	56.7	54.7	55.1	54	4.0112
212	95-4-79.	57.1	56.7	58.1	59.6	57.1	59.8	58.1	1.3486
213	91-1-80.	50	61.3	56.5	55.7	55.6	54.2	55.6	3.6501
214	93-2-80.	52.7	56.9	58.9	58.9	56.9	55.3	56.6	2.352
215	86-1-81.	52	49.8	55.1	54.4	56.1	54.2	53.6	2.3022
216	88-2-81.	55.1	57.1	57.1	59.6	63.6	55.1	57.9	3.2352
217	90-3-81.	55.3	56.5	61.7	55.5	60.2	55.1	57.4	2.8442
218	96-4-81.	57.5	55.7	52	56.1	57.1	56.9	55.9	2.0144
219	92-1-82.	59.1	60.4	61.7	59.1	59.6	62	60.3	1.2828
220	94-2-82.	57.7	62.7	59.1	58.3	54.7	60.9	58.9	2.7539
221	97-1-83.	50.8	51.9	52.9	52.7	53.3	51.5	52.2	0.9475
222	99-2-83.	54.2	54.2	56.7	57.7	57.7	54.2	55.8	1.7725
223	101-3-83	52.6	55.5	57.5	58.7	56.3	54.7	55.9	2.147
224	107-4-83	58.7	57.9	60.6	62.4	57.5	57.3	59.1	2.0265
225	103-1-84	53.1	53.8	54.7	54.2	53.5	53.5	53.8	0.5727
226	105-2-84	57.3	57.9	55.7	55.7	55.5	56.7	56.5	0.9913
227	98-1-85.	52.2	56.1	55.7	55.9	55.1	54	54.8	1.4962
228	100-2-85	55.3	55.7	58.9	57.5	59.1	58.1	57.4	1.6083
229	102-3-85	51.5	54.6	53.3	58.7	55.5	54.2	54.6	2.4114
230	108-4-85	59.5	60.6	60.6	57.5	57.5	60.6	59.4	1.5198
231	104-1-86	58.3	60.6	59.6	61.3	61.7	61.3	60.5	1.2941

	Sample	Hv10 test data.							
	#	1	2	3	4	5	6	AVE	STD. DEV.
232	106-2-86	61.1	63.6	63.6	60.4	66	42	59.5	8.7804
233	121-1-87	48.9	53.8	52.7	52.6	54	50.3	52.1	2.0285
234	123-2-87	53.3	53.6	51.5	52.7	51.9	50.3	52.2	1.2336
235	125-3-87	51.5	50.5	53.1	53.5	54.9	54	52.9	1.6327
236	131-4-87	51.9	55.9	57.3	55.5	55.7	54.4	55.1	1.8291
237	128-1-88	60	59.1	57.9	47.8	54.2	57.5	56.1	4.5146
238	130-2-88	57.5	62.7	55.5	58.5	60.2	58.9	58.9	2.4417
239	122-1-89	52.6	54.4	55.1	56.1	55.5	54.7	54.7	1.2044
240	124-2-89	53.8	56.3	54.7	51.5	56.3	55.3	54.7	1.8174
241	126-3-89	51.9	55.2	54	51	54.2	52.9	53.2	1.5659
242	132-4-89	54.2	55.3	55.1	57.9	56.9	63.6	57.2	3.4221
243	127-1-90	52.2	61.3	56.3	54.6	55.5	54.7	55.8	3.0395
244	129-2-90	53.3	52.2	57.1	58.1	59.8	55.9	56.1	2.8904
245	133-1-91	50.7	49.3	52.6	50.5	50.8	49.2	50.5	1.2384
246	137-2-91	52.9	51.9	55.3	52.9	54.7	54	53.6	1.275
247	139-1-92	50.8	50.2	51.9	52.4	52.6	55.1	52.2	1.7119
248	141-2-92	54.9	52.6	54.7	57.1	57.5	54.7	55.3	1.8019
249	140-1-93	56.5	56.9	56.3	60.4	56.5	59.6	57.7	1.81
250	142-2-93	61.1	55.1	57.3	62.9	60	60.2	59.4	2.794
251	131-1-94	53.1	54	54.4	51.9	56.3	53.6	53.9	1.4662
252	136-2-94	55.9	57.3	55.3	51.8	58.1	56.1	55.8	2.1852
253	138-3-94	51.9	52	54.2	54	51.9	51.5	52.6	1.189
254	144-4-94	56.1	58.3	59.8	60.4	61.3	59.1	59.2	1.8239
255	169-1-95	52	51.3	48.7	48.2	46.7	49.5	49.4	1.9799
256	170-2-95	51.3	52.7	51.1	51.3	52	51.3	51.6	0.6145
257	171-1-96	48.9	53.6	51.3	50.8	50.8	48.9	50.7	1.7475
258	172-2-96	43.6	49.3	50.3	47.8	47.3	48.2	47.8	2.3037
259	200-1-97	51.5	54.6	51.9	52.6	51	50.2	52	1.524
260	201-2-97	48.6	47.9	49.5	49.7	50	51.5	49.5	1.2372
261	199-1-98	49.7	49	49	49.5	47.9	48.2	48.9	0.7083
262	203-2-98	49	48.4	49	48.6	48.6	47.6	48.5	0.5164
263	177-1-99	47.9	47.6	47.5	46.7	47.8	46.1	47.3	0.7118
264	178-2-99	46.9	46.3	45.7	46.1	46.1	46.4	46.3	0.3987
265	79-1-10	49.5	47.9	46.7	47	46	45	47	1.5587
266	81-2-10	42.7	45.6	45.8	47	46.3	45	45.4	1.4846
267	97-1-10	54.9	53.1	55.3	58.9	58.9	58.1	56.5	2.4345
268	98-2-10	56.1	55.9	59.1	57.1	56.1	56.5	56.8	1.205
269	85-1-10	62.9	59.8	58.3	59.3	59.1	61.1	60.1	1.6618
270	86-2-10	63.6	61.3	60	60.4	62.9	61.5	61.6	1.3992
271	14-1-103	53.6	52.4	51.5	53.1	51.9	52.6	52.5	0.7679
272	18-2-103	53.8	54.6	54.2	54.4	55.1	52.9	54.2	0.7554
273	16-1-104	53.3	52.9	54.2	51.7	53.8	54.2	53.4	0.9566
274	22-2-104	55.7	58.7	56.7	55.9	57.1	58.5	57.1	1.2712
275	57-1-105	54.4	52.7	54.9	49.3	54.6	54.7	53.4	2.1759
276	58-2-105	57.1	56.3	55.1	58.1	58.3	57.3	57	1.1911
277	52-1-106	52.4	49.7	49.8	50.3	51.5	49.8	50.6	1.1161
278	70-2-106	60	55.1	56.3	56.9	55.7	59.1	57.2	1.9498
279	25-1-107	48.2	48.2	49.3	49.2	47.8	47	48.3	0.8681
280	31-2-107	54	55.5	54.6	52.7	54.2	55.1	54.4	0.9813

	Sample	Hv10 test data.							
	#	1	2	3	4	5	6	AVE	STD. DEV.
281	50-1-108	47.5	48.2	49	49.8	49.5	49.8	49	0.9395
282	58-2-108	55.9	57.1	57.1	57.1	57.9	58.7	57.3	0.9381
283	57-1-109	57.7	52.9	53.3	54.6	55.5	58.3	55.4	2.2364
284	71-2-109	56.3	54.7	55.7	56.9	53.8	54	55.2	1.2644
285	91-1-110	54	54.9	53.1	55.5	51.5	51.9	53.5	1.608
286	93-2-110	52.7	52	54.2	56.5	53.6	52	53.5	1.7111
287	73-1-11	48.7	51.5	50.3	50.7	50.5	49.5	50.2	0.9778
288	74-2-11	49.3	46.4	47.9	47	49	48.9	48.1	1.1856
289	82-1-11	45.7	46.6	46.9	46.7	46.9	45.8	46.4	0.5428
290	83-2-11	45.3	47.3	47.6	46.6	47	45.3	46.5	0.9988
291	85-1-11	61.1	60.4	52.4	52.6	58.1	56.5	56.9	3.7474
292	86-2-11	55.7	55.7	57.3	62.2	57.9	57.7	57.8	2.3847
293	75-1-11	46.4	47.8	48.4	48.9	48.4	49.3	48.2	1.0178
294	76-2-11	48.2	48.6	48.6	48.6	47.8	48.2	48.3	0.3266
295	80-1-11	45.3	45.1	44.4	43.8	44.6	44.9	44.7	0.5419
296	82-2-11	46.7	45.1	44.6	46.3	46.3	45.6	45.8	0.8091
297	89-1-11	53.6	57.5	57.7	57.7	58.7	56.7	57	1.7759
298	90-2-11	54.4	55.1	56.3	54.7	57.1	56.1	55.6	1.0477
299	92-1-11	59.1	59.1	57.5	57.3	59.3	57.3	58.3	0.9913
300	93-2-11	56.3	57.5	57.1	57.5	59.8	62	58.4	2.1276
301	94-1-11	58.3	57.1	56.2	57.1	57.9	58.7	57.6	0.9203
302	95-2-11	57.1	56.7	57.1	54.9	61.3	58.7	57.6	2.1676
303	97-1-11	50.7	54.2	57.1	59.1	60.6	60.6	57.1	3.946
304	98-2-11	58.7	60.4	63.5	60.9	56.1	62.8	60.4	2.7203
305	54-1-12	54.7	55.5	57.3	58.3	57.3	55.5	56.4	1.3952
306	91-2-12	59.1	57.7	55.7	55.7	55.5	56.9	56.8	1.4292
307	92-1-121	60.6	59.6	58.4	60.9	59.3	58.6	59.6	1.0211
308	08-2-12	56.5	60.9	59.8	58.1	60.6	60.4	59.4	1.7291
309	03-1-12	55.7	54	54.9	57.7	55.3	54.2	55.3	1.3401
310	07-2-12	53.6	57.1	58.7	57.9	60	56.1	57.2	2.225
311	73-1-12	45.7	48.2	47.9	49.2	48.6	49.2	48.1	1.3018
312	74-2-12	45.7	43.6	48.2	49.3	49.3	46.7	47.1	2.2474
313	41-1-124	50	49	47.6	47	47.5	47	48	1.2172
314	60-2-124	57.7	58.1	59.1	56.9	56.3	57.1	57.5	0.9913
315	95-1-12	54.2	57.9	62.2	59.6	59.1	64.3	59.6	3.4967
316	98-2-12	57.5	53.8	59.1	63.1	56.1	60.9	58.4	3.3493
317	84-1-12	61.7	61.3	61.1	61.7	59.1	65	61.7	1.9055
318	89-2-12	57.7	55.5	57.9	60.2	59.6	59.3	58.4	1.7108
319	82-1-12	47.9	46.7	46.7	47.2	48.5	46.4	47.2	0.814
320	83-2-12	46.7	49	49.2	49.3	48.7	49.2	48.7	0.9948
321	80-1-12	47.9	45.6	46.7	46.7	48.2	48.2	47.2	1.0534
322	64-2-12	58.5	59.3	58.1	60	58.3	59.1	58.9	0.7167
323	73-1-12	53.3	48.7	50.2	50.2	50.5	48.1	50.2	1.8085
324	46-2-12	50.7	55.1	55.9	57.5	54.6	55.9	55	2.3028
325	41-1-130	49.2	48.1	46.1	45.7	46.4	46	46.9	1.4049
326	60-2-130	59.1	58.5	56.5	57.5	57.1	55.9	57.4	1.2044
327	81-1-131	52.9	54.2	54.2	56.7	56.5	55.1	54.9	1.4706
328	88-2-13	61.1	59.1	57.7	59.1	59.6	61.3	59.7	1.359
329	20-1-13	60.2	57.1	59.1	57.1	58.3	61.1	58.8	1.6351

	Sample	Hv10 test data.							
	#	1	2	3	4	5	6	AVE	STD. DEV.
330	89-2-13	66.8	60.9	58.5	63.6	62.7	59.8	62.1	2.9791
331	73-1-13	49.8	51.5	51.2	51.5	51	48.2	50.5	1.3049
332	53-2-13	51.5	51.9	51.5	51.9	51.2	50.7	51.5	0.455
333	41-1-134	49.5	48.7	48.9	49.5	49.3	47.6	48.9	0.7223
334	60-2-134	49.3	52.7	56.7	52.7	53.5	53.1	53	2.3588
339	73-1-13	47.9	48.6	49.7	50.7	49.5	46.3	48.8	1.5497
340	12-2-13	50.3	50.7	50.3	48.9	50.8	49.8	50.1	0.7005
341	24-1-13	47.5	50.2	49	52.2	51.9	49.3	50	1.8016
342	27-2-13	49.5	54.7	51.7	53.1	55.1	49	52.2	2.5787
335	52-1-13	54.2	57.5	50.2	51.7	51.7	56.7	53.7	2.9642
336	89-2-13	57.5	56.5	54.6	58.3	55.5	59.6	57	1.8417
337	61-1-13	53.5	50.5	53.8	52.2	52.9	52.7	52.6	1.1764
338	64-2-13	53.1	53.1	51.7	52.7	53.8	53.5	53	0.7333
343	18-1-13	51.5	53.5	56.3	53.8	51.3	50.5	52.8	2.1433
344	33-2-13	49	52.2	54.9	54.6	52.2	51.2	52.4	2.198
345	38-1-14	51.2	49.7	48.7	49.2	49.7	47.2	49.3	1.3197
346	40-2-14	51.2	52	49.3	50.3	41.8	48.6	48.9	3.6746
347	55-1-14	49.3	50.8	50.3	51.3	48.2	50.8	50.1	1.1583
348	58-2-14	53.1	47.8	47.6	48.2	50.2	51.9	49.8	2.3178
349	74-1-14	52.2	50.5	51.7	52	54	52.9	52.2	1.1754
350	78-2-14	60.2	60.9	60.2	60.9	61.3	58.9	60.4	0.8532
351	75-1-14	48.9	49.3	50.3	49.8	48.6	51.2	49.7	0.9621
352	79-2-14	55.9	57.1	55.5	54.4	56.1	57.5	56.1	1.1179
353	76-1-14	50.3	52.4	50.5	47.2	50.8	50.3	50.3	1.6909
354	80-2-14	63.8	55.5	57.1	57.9	56.5	56.9	58	2.9717
355	36-1-14	49.8	48.6	50	49.7	50.2	48.7	49.5	0.6812
356	64-2-14	60.4	51.2	62	49.8	58.7	59.1	56.9	5.084
357	28-1-148	52.2	54.4	52.4	52.6	52.9	50.8	52.6	1.1623
358	60-1-149	52.9	58.3	56.7	56.9	57.7	59.6	57	2.2737
359	32-1-150	55.1	57.5	57.5	56.1	57.7	59.1	57.2	1.3895
360	34-1-15	52.4	56.5	54.4	60.2	52.9	55.9	55.4	2.8548
361	15-1-15	50.2	48.2	47.6	51.7	47.5	46.7	48.7	1.9045
362	21-2-15	49.5	49.5	50.8	48.6	46.9	48.1	48.9	1.3461
363	30-1-15	52.7	55.1	52.9	53.3	52	50.7	52.8	1.4566
364	33-2-15	50	51.5	54	53.6	51	49.2	51.6	1.9202
365	06-1-15	48.9	48.6	47.3	50.3	50	49.2	49.1	1.0747
366	58-2-15	50	48.1	50.7	48.1	47	48.9	48.8	1.3624
367	40-1-15	47.9	47.9	47.6	47.5	47.8	47	47.6	0.343
368	09-1-15	43.6	46.9	46.9	44.8	43.4	47.6	45.5	1.8349
369	74-1-15	51.5	47.2	47	46.4	47	46.9	47.7	1.897
370	78-2-15	61.3	57.9	57.3	56.5	57.9	60.9	58.6	1.9826
371	75-1-15	47.5	48.6	49.3	48.9	49	46	48.2	1.2513
372	21-1-15	48.6	49.5	47.5	47.9	49.5	48.2	48.5	0.8311
373	79-2-15	57.5	58.3	59.6	59.6	55.9	56.5	57.9	1.5531
374	33-1-15	50	51	54	50.5	50.5	50.2	51	1.4922
375	58-1-15	48.4	52	54.7	54.2	52	49.2	51.8	2.5517
376	64-1-15	54.7	55.7	56.5	57.1	55.3	59.1	56.4	1.5735
377	75-1-16	50.5	49.8	51	49.8	50.5	48.4	50	0.9099
378	79-1-16	55.1	58.9	54.4	57.3	58.1	58.3	57	1.8422

	Sample	Hv10 test data.							
	#	1	2	3	4	5	6	AVE	STD. DEV.
379	92-1-16	58.9	59.3	53.6	50.7	52.2	54.4	54.9	3.5275
380	89-1-16	57.3	54	51.9	54.4	55.5	55.5	54.8	1.8129
381	93-1-16	59.6	58.3	57.3	56.7	55.5	55.9	57.2	1.5368
382	78-1-16	59.1	57.5	56.7	58.3	54.6	51	56.2	2.9786
383	91-1-16	55.5	49	51.9	52.7	51.7	52.9	52.3	2.1056
384	83-1-16	48.2	50.7	49	49.2	51.5	49	49.6	1.2377
385	69-1-16	50.8	50.5	46.9	51	50.8	50.8	50.1	1.5921
386	33-1-16	52.4	49.3	54.4	54	52.7	49.8	52.1	2.1204
387	58-1-17	51.5	49.8	53.3	52	51.5	51.5	51.6	1.1243
388	77-1-17	47	47.8	47	45.8	47.8	46.6	47	0.7589
389	69-1-17	47.3	45.1	49.8	49.5	47.9	47.6	47.9	1.7002
390	69-1-17	47.5	48.9	46.3	47	47.5	48.9	47.7	1.04
391	82-1-17	49.7	48.9	49	47.8	47.2	48.9	48.6	0.9109
392	05-1-17	44	47.6	47	47.3	47	46.3	46.5	1.314
393	78-1-17	58.5	56.1	56.7	56.5	60	54.4	57	1.9572
394	69-1-17	48.9	48.9	47.5	47.8	48.6	47.6	48.2	0.6555
395	07-1-17	46.7	45.3	47	47.2	46.7	46.6	46.6	0.6676
396	08-1-17	45.3	47.2	49	47.3	47.2	47.2	47.2	1.1713
397	11-1-18	50.7	49.8	50.7	49.2	49.8	48.7	49.8	0.7985
398	14-1-18	47.2	49.8	48.9	47.3	48.1	47.3	48.1	1.0602
399	17-1-18	52.2	52.4	52.6	55.5	54.6	49.5	52.8	2.0967
400	20-1-18	52.2	49.8	48.7	54.2	51.7	55.5	52	2.567
401	25-1-18	49.3	51	50.5	52.4	51.2	51	50.9	1.008
402	07-1-18	46.4	47	50.3	47.8	48.6	46.3	47.7	1.5306
403	11-1-18	51	47.5	52.7	51.9	45.3	48.7	49.5	2.847
404	14-1-18	49.5	48.6	48.2	47.3	50	49.2	48.8	0.9737
405	33-1-18	50.2	52.4	48.9	49.3	49.7	49.2	50	1.2818
406	26-1-18	48.9	53.6	51.7	53.1	51	49	51.2	1.9894
407	29-1-19	51.5	53.1	52.9	56.5	52	50.8	52.8	2.006
408	32-1-19	49.3	50.3	52.4	49.3	49.3	50.7	50.2	1.2271
409	35-1-19	46.7	48.2	45	46.7	46.9	48.6	47	1.2797
410	39-1-19	49.8	48.7	47.3	48.7	50.5	49.3	49.1	1.0986
411	51-1-19	49.5	50.7	51.7	48.2	48.7	50.5	49.9	1.3212
412	54-1-19	50.2	50	51.3	52.2	50.2	50.3	50.7	0.8672
413	57-1-19	53.8	53.8	50	53.3	51	51.7	52.3	1.6021
414	63-1-19	53.1	51.9	52.9	51.3	52.2	51.9	52.2	0.6765
415	67-1-19	51	49.7	48.4	48.9	48.7	48.7	49.2	0.9709
416	73-1-19	53.6	52.9	55.5	53.1	55.1	54.9	54.2	1.1179
417	60-1-20	52.2	50.8	51.2	50.5	50.2	46.7	50.3	1.8801
418	33-1-20	49.8	51.9	52.7	54.6	55.5	52.4	52.8	2.0253
419	13-1-20	54	53.3	54.9	53.3	53.1	52.4	53.5	0.8556
420	16-1-20	49.8	48.4	50.2	49.3	49.3	49	49.3	0.625
421	85-1-20	47.8	47.8	49	49	51	47.5	48.7	1.306
422	70-1-20	57.9	58.3	57.9	56.7	61.3	54.7	57.8	2.1606
423	71-1-20	58.1	54.7	55.5	58.9	56.9	53.3	56.2	2.1229
424	07-1-20	48.2	48.2	48.9	48.1	47.3	49.8	48.4	0.8472
425	10-1-20	45.8	45.8	45.7	45.7	46	44.6	45.6	0.502
426	33-1-20	51.7	54.2	54.7	51.7	51.5	54.9	53.1	1.6425
427	39-1-21	47.9	49.2	49.5	47.6	47.3	48.2	48.3	0.8841

	Sample	Hv10 test data.							
	#	1	2	3	4	5	6	AVE	STD. DEV.
428	51-1-21	50.5	50.5	51.2	51.7	50.7	50.3	50.8	0.5307
429	60-1-21	51.5	44.4	50.3	50	50	51	49.5	2.5843
430	67-1-21	49.5	48.9	49.5	48.1	48.6	49.5	49	0.5879
431	69-1-21	47	47	45.1	51.9	52.2	52.6	49.3	3.2948
432	75-1-21	51.7	47.9	50.5	49.7	49.2	50.8	50	1.3352
433	89-1-21	57.1	58.1	56.9	60.9	57.1	59.6	58.3	1.6327
434	07-1-21	47.9	47.6	46.7	47.5	48.2	47.5	47.6	0.5046
435	10-1-21	49.5	47.3	45.4	44.7	46	45.8	46.5	1.7213
436	72-1-21	57.1	56.7	50.2	59.2	54.7	59.8	56.3	3.4994
437	40-1-22	49.7	50.2	50.2	48.6	51.9	50.8	50.2	1.1003
438	58-1-22	53.5	50	54.6	52.2	52.2	53.1	52.6	1.5582
439	13-1-22	50.5	52.9	51.5	54.2	52.6	51.5	52.2	1.3054
440	19-1-22	52.2	53.8	54.4	55.9	53.6	50.3	53.4	1.9232
441	22-1-22	50.2	50.2	51.7	51.2	50.2	49.5	50.5	0.8
442	25-1-22	51.5	51	50.7	50.5	49.7	55.3	51.5	1.9776
443	28-1-22	51.5	53.1	51.2	52.4	54.2	52.9	52.6	1.1041
444	33-1-22	49.5	53.5	54.6	54.4	52.9	51	52.7	2.0147
445	34-1-22	48.6	54.9	53.5	55.3	53.6	55.4	53.6	2.5618
446	31-1-22	54	53.5	52.2	52.4	56.3	51.7	53.4	1.679
447	37-1-23	49.3	50.5	51.2	49.5	52.2	50.7	50.6	1.0801
448	40-1-23	51.3	51.2	51.3	50.7	51.5	50.7	51.1	0.3371
449	50-1-23	55.1	54	56.7	54.9	52.7	49.2	53.8	2.5967
450	51-1-23	52.2	47.9	48.9	48.6	52.7	50.2	50.1	1.9854
451	53-1-23	57.1	55.5	54.9	52.9	58.5	53.8	55.5	2.0763
452	56-1-23	50	49.2	51.2	50.7	52	50.3	50.6	0.973
453	89-1-23	58.3	56.9	55.3	60.2	60.9	66.3	59.7	3.8573
454	59-1-23	49.5	49.7	51.5	50.3	49.8	48.9	50	0.8849
455	60-1-23	49	50.3	48.6	48.7	50.8	49.5	49.5	0.8976
456	81-1-23	52.9	51.3	54.2	57.5	52	52.6	53.4	2.223
457	62-1-24	50.2	52.2	52.2	49.2	50.8	51	50.9	1.1639
458	65-1-24	55.5	53.6	58.1	56.3	53.3	55.1	55.3	1.7781
459	77-1-24	47.2	46.7	47.2	46.7	48.9	50	47.8	1.3556
460	75-1-24	48.7	49.3	49.2	49.3	51.7	49.7	49.7	1.054
461	76-1-24	51.5	49.2	47.3	47.5	48.6	46.7	48.5	1.742
462	79-1-24	56.1	53.3	51.2	55.7	54.2	55.9	54.4	1.9142
463	80-1-24	62.2	54	52.2	57.3	57.1	56.7	56.6	3.4126
464	82-1-24	47.5	50.5	48.7	48.2	49.5	49.8	49	1.1057
465	84-1-24	46.9	47.8	50.2	49	49.2	49.3	48.7	1.1827
466	83-1-24	48.9	48.7	49.3	48.7	47.9	48.6	48.7	0.4579
467	86-1-25	46.7	47.9	47.6	47.6	47.6	45.1	47.1	1.0534
468	87-1-25	51	51.2	52.7	49.5	47.8	50.3	50.4	1.6654
469	93-1-25	51.2	54	55.1	54.2	55.5	53.3	53.9	1.5329
470	91-1-25	51.5	52.6	49.7	53.6	54.4	53.1	52.5	1.675
471	92-1-25	57.9	55.7	55.7	52.9	58.9	54.6	56	2.1797
472	34-1-25	49.2	47.5	51	51	48.6	50.5	49.6	1.4348
473	37-1-25	49.7	48.9	49	49	49.8	47.6	49	0.7874
474	51-1-25	55.1	53.3	54.4	53.1	51.7	52.2	53.3	1.2853
475	56-1-25	52	47.9	50.2	48.1	49.8	48.7	49.5	1.5476
476	59-1-25	49.5	49.5	50.5	49.8	51.2	53.5	50.7	1.5371

	Sample	Hv10 test data.							
	#	1	2	3	4	5	6	AVE	STD. DEV.
477	60-1-26	52.9	48.6	50.5	47.5	49.7	48.7	49.7	1.8929
478	81-1-26	54.9	53.1	56.1	55.5	51.9	55.5	54.5	1.6395
479	34-1-26	51.5	53.3	55.5	55.1	50.5	51	52.8	2.147
480	51-1-26	53.8	53.6	52	52.9	54.6	56.3	53.9	1.4801
481	56-1-26	51.2	53.1	52.6	51.5	54.6	52.7	52.6	1.2189
482	59-1-26	49.2	52.6	52	50.2	50.2	48.9	50.5	1.4892
483	75-1-26	50.8	53.1	52.2	52.6	51.7	50.8	51.9	0.9459
484	76-1-26	49.2	51.5	53.8	49.2	53.7	53.3	51.8	2.1665
485	79-1-26	60.9	57.3	56.5	54.9	57.1	59.1	57.6	2.0963
486	94-1-26	51.7	51.5	51.7	52.2	52.2	51.2	51.8	0.3937

	Sample	Hv10 test data.							
	#	1	2	3	4	5	6	AVE	STD. DEV.
487	RM10	55.1	56.3	57.5	58.5	58.9	54.9	56.9	1.7037
488	RM11	52.7	50.5	53.1	52	52.6	50.2	51.9	1.2178
489	HAM1	49.8	52.9	53.3	52.7	53.3	50	52	1.6444
490	AX65	49	49.7	50.2	49	51.5	51.2	50.1	1.0733
491	RMF	51.3	57.9	54.9	50.2	55.1	55.1	54.1	2.833
492	RMG	51.5	58.9	51.7	50.7	56.9	47.5	52.9	4.2283
493	RMX	41.3	51.9	54.4	56.9	54.2	58.3	52.8	6.0767
494	RMY	49.2	48.6	50.8	53.3	51	48.6	50.3	1.8284
495	RMZ	45.1	45.3	45.8	51.5	47.5	45.4	46.8	2.4768

Appendix L

ASTM Grain Size Results.

	SAMPLE #	Grain Size ASTM. (G(M))
1	37-1-2	8.05
2	43-2-2	8.05
3	44-3-2	7.55
4	48-4-2	7.8
5	61-1-3	8.3
6	67-2-3	6.8
7	68-3-3	7.3
8	72-4-3	6.8
9	1-1-4	7.3
10	7-2-4	8.8
11	8-3-4	7.3
12	12-4-4	7.05
13	109-1-5	8.4
14	120-2-5	7.8
15	97-1-6	7.8
16	108-2-6	7.3
17	169-1-7	7.8
18	170-2-7	7.3
19	171-3-7	7.3
20	172-4-7	7.05
21	188-1-8	7.8
22	189-2-8	7.8
23	190-3-8	7.3
24	191-4-8	7.8
25	180-1-9	7.05
26	181-2-9	6.3
27	182-3-9	6.8
28	183-4-9	6.3
29	204-1-10	7.95
30	205-2-10	12.55
31	1-1-11	7.55
32	7-2-11	6.55
33	9-3-11	6.3
34	11-4-11	7.3
35	2-1-12	7.3
36	4-2-12	6.3
37	6-3-12	6.3
38	12-4-12	8.3
39	3-1-13	7.05
40	5-2-13	7.3
41	8-1-14	7.3
42	10-2-14	6.3
43	37-1-15	6.8

	SAMPLE #	Grain Size ASTM. (G(M))
44	43-2-15	7.8
45	45-3-15	5.55
46	47-4-15	5.55
47	38-1-16	8.3
48	40-2-16	5.8
49	42-3-16	7.3
50	48-4-16	7.55
51	39-1-17	7.3
52	41-2-17	8.05
53	44-1-18	6.3
54	46-2-18	7.3
55	73-1-19	8.3
56	79-2-19	8.3
57	81-3-19	8.8
58	83-4-19	7.8
59	74-1-20	8.3
60	76-2-20	9.3
61	78-3-20	8.8
62	84-4-20	8.3
63	75-1-21	8.4
64	77-2-21	8.9
65	80-1-22	7.9
66	82-2-22	9.05
67	110-1-23	9.4
68	112-2-23	8.8
69	114-3-23	9.4
70	120-4-23	9.65
71	10-1-24	8.05
72	12-2-24	7.9
73	118-1-25	7.2
74	120-2-25	7.3
75	79-1-26	9.05
76	81-2-26	8.3
77	83-3-26	8.2
78	84-4-26	8.4
79	159-1-27	7.3
80	195-2-27	7.8
81	4-1-28	7.3
82	12-2-28	6.8
83	157-1-29	7.55
84	160-2-29	7.8
85	77-1-30	7.8
86	84-2-30	8.3

	SAMPLE #	Grain Size ASTM. (G(M))
87	109-1-31	8.3
88	115-2-31	7.8
89	117-3-31	8.3
90	120-4-31	7.8
91	38-1-32	7.3
92	40-2-32	7.3
93	46-3-32	6.8
94	48-4-32	7.3
95	1-1-33	7.05
96	2-2-33	8.55
97	6-3-33	6.55
98	12-4-33	6.8
99	3-1-34	7.8
100	5-2-34	7.05
101	7-1-35	7.3
102	9-2-35	7.05
103	8-1-36	7.3
104	24-2-36	7.55
105	11-1-37	7.05
106	35-2-37	8.9
107	123-1-38	7.95
108	135-2-38	10.4
109	143-3-38	9.55
110	144-4-38	8.7
111	37-1-39	7.55
112	39-2-39	8.05
113	41-3-39	8.3
114	42-4-39	7.3
115	43-1-40	8.55
116	44-2-40	7.8
117	45-1-41	7.8
118	47-2-41	6.05
119	74-1-42	8.3
120	76-2-42	7.55
121	78-3-42	7.7
122	84-4-42	11.4
123	75-1-43	7.8
124	81-2-43	8.3
125	79-1-44	8.55
126	80-2-44	8.3
127	82-1-45	8.3
128	94-2-45	8.3
129	83-1-46	7.55

	SAMPLE #	Grain Size ASTM. (G(M))
130	95-2-46	8.8
131	110-1-47	8.2
132	112-2-47	8.4
133	114-3-47	7.8
134	120-4-47	8.55
135	111-1-48	8.05
136	113-2-48	7.7
137	116-1-49	8.3
138	118-2-49	8.05
139	145-1-50	9.3
140	147-2-50	9.55
141	151-1-51	8.05
142	155-2-51	12.4
143	158-1-52	7.8
144	160-2-52	7.3
145	164-1-53	7.8
146	168-2-53	9.8
147	149-1-54	8.05
148	150-2-54	7.8
149	165-1-55	12.4
150	166-2-55	11.15
151	163-1-56	8.05
152	167-2-56	12.9
153	152-1-57	7.8
154	156-2-57	11.9
155	13-1-58	8.8
156	15-2-58	8.3
157	17-3-58	7.3
158	23-4-58	6.8
159	19-1-59	8.05
160	21-2-59	7.55
161	26-1-60	12.4
162	28-2-60	10.3
163	30-3-60	9.3
164	36-4-60	9.8
165	68-1-61	11.4
166	70-2-61	10.9
167	146-1-62	7.8
168	148-2-62	7.3
169	153-1-63	12.4
170	154-2-63	11.9
171	161-1-64	8.05
172	162-2-64	7.8

	SAMPLE #	Grain Size ASTM. (G(M))
173	147-1-65	7.3
174	155-2-65	12.9
175	32-1-66	12.4
176	34-2-66	12.15
177	31-1-67	12.15
178	33-2-67	12.9
179	20-1-68	8.05
180	22-2-68	7.8
181	14-1-69	8.05
182	18-2-69	7.55
183	25-1-70	9.3
184	27-2-70	13.65
185	29-3-70	12.9
186	35-4-70	12.15
187	49-1-72	8.55
188	51-2-72	8.3
189	53-3-72	8.8
190	59-4-72	7.55
191	55-1-73	8.8
192	57-2-73	7.8
193	50-1-74	9.05
194	52-2-74	8.3
195	54-3-74	8.3
196	60-4-74	7.55
197	56-1-75	8.55
198	58-2-75	8.3
199	61-1-76	12.9
200	63-2-76	12.15
201	65-3-76	10.05
202	71-4-76	9.3
203	67-1-77	11.8
204	69-2-77	12.3
205	62-1-78	12.05
206	64-2-78	12.3
207	66-3-78	11.8
208	72-4-78	10.55
209	85-1-79	9.3
210	87-2-79	8.2
211	89-3-79	7.7
212	95-4-79	8.4
213	91-1-80	10.2
214	93-2-80	10.4
215	86-1-81	9.3

	SAMPLE	Grain Size
	#	ASTM. (G(M))
216	88-2-81	8.4
217	90-3-81	7.8
218	96-4-81	8.3
219	92-1-82	9.15
220	94-2-82	8.9
221	97-1-83	11.4
222	99-2-83	11.15
223	101-3-83	10.4
224	107-4-83	9.4
225	103-1-84	12.15
226	105-2-84	11.65
227	98-1-85	11.65
228	100-2-85	10.15
229	102-3-85	10.15
230	108-4-85	9.55
231	104-1-86	11.4
232	106-2-86	11.15
233	121-1-87	8.9
234	123-2-87	8.9
235	125-3-87	8.4
236	131-4-87	7.95
237	128-1-88	8.3
238	130-2-88	8.3
239	122-1-89	8.4
240	124-2-89	8.4
241	126-3-89	8.2
242	132-4-89	8.3
243	127-1-90	8.9
244	129-2-90	8.4
245	133-1-91	12.15
246	137-2-91	11.15
247	139-1-92	11.65
248	141-2-92	10.9
249	140-1-93	11.9
250	142-2-93	10.15
251	131-1-94	8.2
252	136-2-94	10.9
253	138-3-94	10.4
254	144-4-94	10.3
255	169-1-95	6.45
256	170-2-95	6.8
257	171-1-96	6.3
258	172-2-96	7.05
259	200-1-97	9.3
260	201-2-97	9.8
261	199-1-98	10.3
262	203-2-98	8.3
263	177-1-99	5.8
264	178-2-99	7.8
265	179-1-100	8.3

	SAMPLE	Grain Size
	#	ASTM. (G(M))
266	181-2-100	6.8
267	197-1-101	11.9
268	198-2-101	11.15
269	185-1-102	11.9
270	186-2-102	10.65
271	14-1-103	8.3
272	18-2-103	7.8
273	16-1-104	9.8
274	22-2-104	8.05
275	57-1-105	8.8
276	58-2-105	10.8
277	52-1-106	8.55
278	70-2-106	12.65
279	25-1-107	13.4
280	31-2-107	10.9
281	50-1-108	8.3
282	58-2-108	8.05
283	57-1-109	8.8
284	71-2-109	12.9
285	91-1-110	8.9
286	93-2-110	9.4
287	173-1-111	7.3
288	174-2-111	7.55
289	182-1-112	6.3
290	183-2-112	6.8
291	185-1-113	11.4
292	186-2-113	10.8
293	175-1-114	7.8
294	176-2-114	8.9
295	180-1-115	7.8
296	182-2-115	7.55
297	189-1-116	11.65
298	190-2-116	10.8
299	192-1-117	11.4
300	193-2-117	10.4
301	194-1-118	11.9
302	195-2-118	10.65
303	197-1-119	11.15
304	198-2-119	10.9
305	154-1-120	12.15
306	191-2-120	10.8
307	92-1-121	8.9
308	108-2-121	10.8
309	103-1-122	11.9
310	107-2-122	10.65
311	173-1-123	8.55
312	174-2-123	9.3
313	41-1-124	6.8
314	60-2-124	7.55
315	195-1-125	11.8

	SAMPLE	Grain Size
	#	ASTM. (G(M))
316	198-2-125	10.3
317	184-1-126	11.55
318	189-2-126	11.15
319	182-1-127	7.55
320	183-2-127	7.05
321	180-1-128	6.8
322	164-2-128	8.8
323	173-1-129.	7.55
324	146-2-129	7.8
325	41-1-130	8.55
326	60-2-130	10.5
327	81-1-131	8.15
328	288-2-131.	8.65
329	120-1-132	7.7
330	289-2-132.	10.15
331	173-1-133	7.05
332	153-2-133	11.9
333	41-1-134	7.05
334	60-2-134	7.55
335	173-1-135	9.15
336	212-2-135.	10.9
337	224-1-136.	10.65
338	227-2-136.	8.15
338	252-1-137.	9.05
340	289-2-137.	7.55
341	261-1-138.	7.8
342	264-2-138.	8.3
343	218-1-139.	11.15
344	233-2-139.	11.4
345	238-1-140.	7.95
346	240-2-140.	9.3
347	255-1-141.	9.4
348	258-2-141.	8.3
349	274-1-142.	11.4
350	278-2-142.	9.9
351	275-1-143.	11.9
352	279-2-143.	11.4
353	276-1-144.	10.4
354	280-2-144.	8.65
355	236-1-146.	9.05
356	264-2-146.	8.05
357	28-1-148	11.9
358	60-1-149	8.3
359	32-1-150	12.9
360	134-1-151.	10.05
361	215-1-152.	9.3
362	221-2-152.	8.3
363	230-1-153.	8.9
364	233-2-153.	11.4
365	206-1-154.	8.2

	SAMPLE	Grain Size
	#	ASTM. (G(M))
366	258-2-154.	9.55
367	240-1-154.	7.8
368	209-1-155.	10.55
369	274-1-155.	12.9
370	278-2-155.	11.9
371	275-1-156.	8.9
372	221-1-156.	8.3
373	279-2-156.	8.3
374	233-1-157.	12.15
375	258-1-158.	10.8
376	264-1-159.	9.3
377	275-1-160.	10.4
378	279-1-161.	9.4
379	292-1-162.	9.4
380	289-1-163.	9.55
381	293-1-164.	9.8
382	278-1-165.	11.9
383	291-1-166.	7.8
384	283-1-167.	12.65
385	169-1-168	8.3
386	233-1-169.	10.9
387	258-1-170.	8.8
388	277-1-171.	9.3
389	269-1-172.	8.3
390	269-1-173.	12.8
391	282-1-174.	8.55
392	205-1-175.	13.65
393	278-1-176.	12.15
394	169-1-177.	7.8
395	207-1-178.	9.3
396	208-1-179.	12.4
397	211-1-180.	10.05
398	214-1-181.	9.3
399	217-1-182.	13.4
400	220-1-183.	11.55
401	225-1-184.	9.8
402	207-1-185.	10.3
403	211-1-186.	13.4
404	214-1-187.	12.9
405	233-1-188.	11.4
406	226-1-189.	13.4
407	229-1-190.	11.9
408	232-1-191.	13.4
409	235-1-192.	13.15
410	239-1-193.	13.15
411	251-1-194.	13.9
412	254-1-195.	13.4
413	257-1-196.	13.15
414	263-1-197.	13.15
415	267-1-198.	13.4

	SAMPLE	Grain Size
	#	ASTM. (G(M))
416	273-1-199.	13.4
417	260-1-200.	13.4
418	233-1-201.	10.4
419	213-1-202.	9.4
420	216-1-203.	8.2
421	285-1-204.	9.3
422	270-1-205.	8.3
423	271-1-206.	11.9
424	207-1-207.	10.55
425	210-1-208.	9.3
426	233-1-209.	11.15
427	239-1-210.	12.4
428	251-1-211.	13.9
429	260-1-212.	13.15
430	267-1-213.	12.4
431	269-1-214.	13.4
432	275-1-215.	8.3
433	289-1-216.	7.8
434	207-1-217.	10.3
435	210-1-218.	9.8
436	272-1-219.	14.4
437	240-1-220.	10.8
438	258-1-221.	9.8
439	213-1-222.	10.9
440	219-1-223.	11.9
441	222-1-224.	8.05
442	225-1-225.	8.8
443	228-1-226.	8.3
444	233-1-227.	11.15
445	234-1-228.	8.8
446	231-1-229.	10.9
447	237-1-230.	10.55
448	240-1-231.	8.8
449	250-1-232.	10.15
450	251-1-233.	12.4
451	253-1-234.	8.9
452	256-1-235.	8.55
453	289-1-236.	9.4
454	259-1-237.	7.55
455	260-1-238.	12.15
456	281-1-239.	8.3
457	262-1-240.	7.8
458	265-1-241.	8.8
459	277-1-242.	9.8
460	275-1-243.	8.3
461	276-1-244.	9.3
462	279-1-245.	9.4
463	280-1-246.	9.55
464	282-1-247.	8.15
465	284-1-248.	8.3

	SAMPLE	Grain Size
	#	ASTM. (G(M))
466	283-1-249.	9.3
467	286-1-250.	12.4
468	287-1-251.	10.65
469	293-1-252.	9.55
470	291-1-253.	8.8
471	292-1-254.	9.05
472	234-1-255.	10.9
473	237-1-256.	9.9
474	251-1-257.	13.9
475	256-1-258.	10.3

	SAMPLE	Grain Size
	#	ASTM. (G(M))
476	259-1-259.	9.3
477	260-1-260.	13.65
478	281-1-261.	7.8
479	234-1-262.	11.65
480	251-1-263.	13.9
481	256-1-264.	9.55
482	259-1-265.	9.3
483	275-1-266.	9.3
484	276-1-267.	9.8
485	279-1-268.	10.3

	SAMPLE	Grain Size
	#	ASTM. (G(M))
486	294-1-269.	9.3
487	RM10	7.8
488	RM11	7.05
489	HAM1	9.7
490	AX65	9.9
491	RMF	8.3
492	RMG	9.4
493	RMX	7.9
494	RMY	7.9
495	RMZ	11.4

Appendix M

Tensile Test Results.

	Sample #	Dia. mm	M.Stress MPa	0.2%P.S. MPa	δ Area %	δ Length %
1	37-1-2.	11.3	139.1	90	11.5	10.5
2	43-2-2.	11.3	LOST ON INSTRON			
3	44-3-2.					
4	48-4-2.	11.26	130	61	3	4.4
5	61-1-3.	11.28	132.5	73.1	7.8	7.8
6	67-2-3.	11.3	124.4	103	3.3	4.7
7	68-3-3.	9.96	121			3.8
8	72-4-3.	11.3	123.3	62.5	4.6	3.6
9	1-1-4.	11.26	149	70	8	10.2
10	7-2-4.	11.26	149.5	105	10.7	12.8
11	8-3-4.	11.27	160.9	68	9.5	8.3
12	12-4-4.	11.29	139.1	63.5	7.6	8.8
13	109-1-5.	11.28	133.2	66.1	9.3	5.6
14	120-2-5.	11.28	136.5	100	4.5	2.4
15	97-1-6.	11.26	131			3.9
16	108-2-6.	11.28	134.6	116	1.4	3.7
17	169-1-7.	11.31	109	70		
18	170-2-7.	11.28	LOST ON INSTRON			4.6
19	171-3-7.	11.26	128.2	87	8.7	8.5
20	172-4-7.	11.28	165.1	68.5	18.1	11.7
21	188-1-8.					
22	189-2-8.	11.27	153.1	80.7	6.5	6.5
23	190-3-8.	11.3	148.8	74.2	5.8	7.2
24	191-4-8.	11.27	139.1		10.3	9
25	180-1-9.	11.27	136.9	62.4	7.9	7.5
26	181-2-9.	11.28	130	120	10	6.1
27	182-3-9.	11.3	134.6	95	1.4	3.7
28	183-4-9.	11.26	135	90	8	6.5
29	204-1-10.	11.3	118	82	1.4	3.6
30	205-2-10.	11.28	125.6	65	4.4	4.1
31	1-1-11.	11.31	145.6	87	18.7	11.8
32	7-2-11.	11.27	141.4	85.6	7	6.6
33	9-3-11.	11.29	133.2	63.1	10.3	7.3
34	11-4-11.	11.3	126.7	94.2	5.2	6.5
35	2-1-12.	11.31	151.2	98.9	7.8	5.5
36	4-2-12.	11.29	PUNCH FAILURE			
37	6-3-12.	11.28	118.7	75	3.5	4.3
38	12-4-12.	11.3	124.7	102	6.3	5.4
39	3-1-13.	11.3	124.2	72.4	7.6	7.7
40	5-2-13.	11.27	123.5	92.3	3.2	5.7
41	8-1-14.	11.3	119.1	92	3.5	3.5

	Sample #	Dia. mm	M.Stress MPa	0.2%P.S. MPa	δ Area %	δ Length %
42	10-2-14.	11.31	113.6	98	3.5	5.2
43	37-1-15.	11.29	105.3	82	10.3	7.5
44	43-2-15.	11.29	121	87.4	3.5	4.1
45	45-3-15.	11.27	119.4	90.6	6.3	6
46	47-4-15.	11.31	123.5	82	3.6	4.7
47	38-1-16.	11.28	112.9	98	3.5	4.6
48	40-2-16.	11.3	111.9	87	5.1	4.5
49	42-3-16.	11.3	120.4	90	3.5	3.7
50	48-4-16.	11.3	122.2	88.7	4	3.5
51	39-1-17.	11.31	121.4	58.1	8	5.9
52	41-2-17.	11.29	119.5	66	4.9	5.9
53	44-1-18.	11.29	115.3	112	3.2	3.7
54	46-2-18.	11.29	POROSITY FAILURE			
55	73-1-19.	11.27	167.2	128	17.6	12.6
56	79-2-19.	11.32	138.6	128	5.9	3.5
57	81-3-19.	11.29	131.4	118	11.2	8.6
58	83-4-19.	11.31	POROSITY FAILURE			
59	74-1-20.	11.3	179.1	123	6.5	6.8
60	76-2-20.	11.29	118.6		4	2.4
61	78-3-20.	11.31	126.8	110	4.9	4.3
62	84-4-20.	11.32	128	109	7.1	5.2
63	75-1-21.	11.3	122.5	120	6.5	5.9
64	77-2-21.	11.29	122.6	92.5	6.6	3.6
65	80-1-22.	11.28	FAILURE REASON UNKNOWN			
66	82-2-22.	11.29	121.6	116	2.5	2.5
67	110-1-23.	11.3	161.3	101	4.9	4.8
68	112-2-23.	11.31	118.9	118	3.2	3.8
69	114-3-23.	11.32	125	118	3.2	2.5
70	120-4-23.	11.33	113.5	90.3	2	1.8
71	10-1-24.	11.34	144	114	4.4	5.3
72	12-2-24.	11.27	131.5	122	4.9	4.6
73	118-1-25.	11.31	136.7	113	4	2.8
74	120-2-25.	11.3	118.4	108	4.9	3.9
75	79-1-26.	11.24	138.6	75.2	3.7	3.5
76	81-2-26.	11.25	149.7	79.9	4.9	4.5
77	83-3-26.	11.26	145.8	91	3.4	3
78	84-4-26.	11.27	121.8	73	5.8	2.7
79	159-1-27.	11.3	140.7	85.9	6.3	4.9
80	195-2-27.	11.2	127.4	72.6	3.2	3.5
81	4-1-28.	11.24	160	66.5	8.7	6.5
82	12-2-28.	11.22	148.1	110	9.9	6.1

	Sample #	Dia. mm	M.Stress MPa	0.2%P.S. MPa	δ Area %	δ Length %
83	157-1-29.	11	143.8	61.1	15.5	9.4
84	160-2-29.	11.26	145.9	84	15	8.8
85	77-1-30.	11.31	172.4	76.9	10.8	10.7
86	84-2-30.	11.27	165.2	114	4.7	5.7
87	109-1-31.	11.25	127.4	113	6.1	4.8
88	115-2-31.	11.21	125.4	84.3	3.4	4.1
89	117-3-31.	11.2	127.7	66.8	3.5	5
90	120-4-31.	11.18	139.5	122	3.7	4.5
91	38-1-32.	11.28	153.1	84.9	9.3	8.4
92	40-2-32.	11.25	147.6	120	7.8	5
93	46-3-32.	11.24	155	108	7.7	4.3
94	48-4-32.	11.17	149.9	104	8.2	6.8
95	1-1-33.	11.3	153.2	116	20.6	12.9
96	2-2-33.	11.19	164	119	8.6	9.8
97	6-3-33.	11.17	148.9	112	11.5	8.4
98	12-4-33.	11.25	149.8	111	7.7	7.3
99	3-1-34.	11.22	156.9	98.9	12.3	9.6
100	5-2-34.	11.21	166.1	120	19.6	12.3
101	7-1-35.	11.24	143.1	98.3	7.5	8.1
102	9-2-35.	11.23	147.2	104	9	7.4
103	8-1-36.	11.24	157.3	126	6.3	5
104	24-2-36.	11.2	147	93.7	5.1	6.6
105	11-1-37.	11.17	147	104	9.1	8
106	35-2-37.	11.24	161.6	119	9.4	7.5
107	123-1-38.	11.24	138.3	93.4	9.2	7
108	135-2-38.	11.28	126.1	73.3	5.8	3.2
109	143-3-38.	11.19	130.6	98.1	3.9	2.8
110	144-4-38.	11.21	132.3	92.8	3.4	2.6
111	37-1-39.	11.24	135.4	99	11.9	9.5
112	39-2-39.	11.26	144	95	12.4	10.7
113	41-3-39.	VERY EARLY FAILURE				
114	42-4-39.	11.27	134.2	106	8.2	5.3
115	43-1-40.	11.21	127	78.9	4.8	4.9
116	44-2-40.	11.19	141.2	103	6.2	4.6
117	45-1-41.	11.17	127.1	80.7	5.3	5.7
118	47-2-41.	11.12	161.1	95.8	7.8	8
119	74-1-42.	11.28	168.2	105	7.5	7.9
120	76-2-42.	11.25	168.9	102	10.4	7.7
121	78-3-42.	11.36	151.6	112	6.6	5.3
122	84-4-42.	11.25	148.1	106	2.5	4.5
123	75-1-43.	11.26	155.6	96.5	12.2	10.3

	Sample	Dia.	M.Stress	0.2%P.S.	δ Area	δ Length
	#	mm	MPa	MPa	%	%
124	81-2-43.	11.24	142	96.8	7.7	4.3
125	79-1-44.	11.22	143.1	96	4.9	6.7
126	80-2-44.	11.25	169	103	6.5	5
127	82-1-45.	11.28	175.3	103	5.9	5.9
128	94-2-45.	11.31	165.2	105	4.4	4.7
129	83-1-46.	11.31	156.3	93	6.4	6.3
130	95-2-46.	11.24	162	115	7.7	5.1
131	110-1-47.	11.23	119.4	85.8	3	3
132	112-2-47.	11.25	149.7	93.2	4.4	3.7
133	114-3-47.	11.35	126.5	95.2	3.5	3.7
134	120-4-47.	11.2	FAILURE ON MACHINE			
135	111-1-48.	11.18	131.5	77.6	7	6
136	113-2-48.	11.2	140.5	87.1	8.6	6.8
137	116-1-49.	11.26	123.1	71	5.3	3.1
138	118-2-49.	11.26	138.6	80	2.3	3.5
139	145-1-50.	11.17	157.9	68.8	12.8	12.1
140	147-2-50.	11.24	133.3	75	7.8	5
141	151-1-51.	11.15	155.1	70.6	5.8	6.3
142	155-2-51.	11.26	148.7	88.8	6.6	6.7
143	158-1-52.	11.22	149.1	101	5.1	5.1
144	160-2-52.	11	135	90.9	4.1	2.9
145	164-1-53.	11.12	145.3	74.4	3.4	3.9
146	168-2-53.	11.18	144.8	91.4	2.1	2.5
147	149-1-54.	11.19	171.1	80.3	16.3	12.2
148	150-2-54.	11.18	183.2	78.8	14.6	11
149	165-1-55.	11.16	147.4	123	7.7	9.1
150	166-2-55.	11.22	148.3	77	3.9	4.6
151	163-1-56.	11.08	131.1	69.2	4.3	4.6
152	167-2-56.	11.06	137.8	79	3.2	3.8
153	152-1-57.	11.1	178.2	82.6	5.2	5.2
154	156-2-57.	11.22	167.9	91.2	4.8	4.7
155	13-1-58.	11.2	153.7	98.9	13.7	13.3
156	15-2-58.	11.19	141.1	64.3	7.7	8.7
157	17-3-58.	11.26	160	68.5	11.2	12.5
158	23-4-58.	11.1	158.4	73.4	7.2	6.9
159	19-1-59.	11.16	153.8	71.7	7.2	8
160	21-2-59.	11.17	160.9	86.4	7.3	8.1
161	26-1-60.	11.24	163.7	68.9	8.2	8.2
162	28-2-60.	11.23	167.9	69.4	7.2	6.9
163	30-3-60.	11.19	160	70.6	7.7	8.3
164	36-4-60.	11.12	144.4	76.5	4.4	3.9
165	68-1-61.	11.17	142.5	73	4.3	4.1
166	70-2-61.	11.27	146.2	80.3	3.7	3.4
167	146-1-62.	11.3	175.7	86.3	9.2	7.2
168	148-2-62.	11.18	172.2	90.1	5.6	5.3
169	153-1-63.	11.23	169.2	75.3	9.7	9
170	154-2-63.	11.24	164.7	103	8.5	7.7
171	161-1-64.	11.28	150.8	65.2	11.7	10.2

	Sample	Dia.	M.Stress	0.2%P.S.	δ Area	δ Length
	#	mm	MPa	MPa	%	%
172	162-2-64.	11.27	163.6	79.1	9	7.4
173	147-1-65.	11.19	165.3	77.7	16.9	10.1
174	155-2-65.	11.17	167.8	83.1	7.7	5.6
175	32-1-66.	11.24	157.6	90.3	3.9	3.8
176	34-2-66.	11.15	160.6	126	3.6	4
177	31-1-67.	11.18	156.5	87.5	8.7	9.2
178	33-2-67.	11.08	162.3	107	7.6	7.8
179	20-1-68.	11.19	158.6	96.6	5.1	4.6
180	22-2-68.	10.97	166.2	125	4.1	6.2
181	14-1-69.	11.23	166	89	12.6	11.4
182	18-2-69.	11.23	158.4	89.2	11.6	9.7
183	25-1-70.	11.27	159.6	89.6	15.7	12.6
184	27-2-70.	11.26	168.2	94.6	19.4	14.6
185	29-3-70.	11.2	169	78.5	12.8	11.9
186	35-4-70.	11.15	163.2	78.6	6.7	9.3
187	49-1-72.	11.19	141.3	72.1	12.6	8
188	51-2-72.	11.3	155.4	63.9	12.6	9.8
189	53-3-72.	11.22	152.5	86.9	19.1	12
190	59-4-72.	11.07	148	99.8	4.1	4.2
191	55-1-73.	11.17	147.9	98.9	6.5	5.9
192	57-2-73.	11.15	133.5	75.6	5.5	4.1
193	50-1-74.	11.28	151.6	74.5	8.5	7.3
194	52-2-74.	11.22	151.8	88.2	8	7
195	54-3-74.	11.24	148.1	104	12.6	6.9
196	60-4-74.	11.12	135.4	89.8	3.4	2.7
197	56-1-75.	11.2	158	85.4	5	5.1
198	58-2-75.	11.01	145.4	91.9	4.7	4.2
199	61-1-76.	11.19	144.1	70.7	10.8	8.6
200	63-2-76.	11.18	151.4	68.9	10.1	9.8
201	65-3-76.	11.09	148.2	103	9.2	8.6
202	71-4-76.	11.01	141.1	81.7	1.3	3.7
203	67-1-77.	10.92	125.6	82.3	3.4	4
204	69-2-77.	11.08	137.9	83.8	4.8	4.6
205	62-1-78.	11.09	156.9	98.8	8.3	6.5
206	64-2-78.	11.07	157.7	74.2	6	5.2
207	66-3-78.	11	151.2	86.2	6.6	5.9
208	72-4-78.	11.15	136.9	87	4.1	3.2
209	85-1-79.	11.24	168.3	82.3	12.1	8.5
210	87-2-79.	11.22	176	94.1	11.8	9.2
211	89-3-79.	11.23	172.2	83.7	8.9	6.8
212	95-4-79.	11.11	169.9	110	7.2	5.5
213	91-1-80.	11.06	135.3	91.6	2.9	3
214	93-2-80.	11.04	145.6	93.1	4.3	4.5
215	86-1-81.	11.24	182.2	93.3	7	6.7
216	88-2-81.	11.16	182.7	125	2.8	4.1
217	90-3-81.	11.18	163.4	124	3.4	4.7
218	96-4-81.	11.02	159.4	105	3.6	4
219	92-1-82.	11.14	167.6	91.3	2.5	3.8

	Sample	Dia.	M.Stress	0.2%P.S.	δ Area	δ Length
	#	mm	MPa	MPa	%	%
220	94-2-82.	11.1	160.2	125	1.8	2.8
221	97-1-83.	11.18	166.3	77.4	14.1	11.3
222	99-2-83.	11.18	160.6	119	7	6.1
223	101-3-83.	11.22	140.8	105	3.9	2.4
224	107-4-83.	11.02	130.6	105	2	2.2
225	103-1-84.	11.21	169.7	91.1	7.7	5.2
226	105-2-84.	11.2	170.6	88	5.4	4.9
227	98-1-85.	11.03	148.9	93	7.5	6.7
228	100-2-85.	11.09	157.8	86.4	7.3	5
229	102-3-85.	11.24	145.1	92.2	4.2	4.5
230	108-4-85.	11.06	128.7	87.2	0.5	1.8
231	104-1-86.	11.13	183.1	95.3	5.8	5.5
232	106-2-86.	11.18	161.4	107	2.5	3.1
233	121-1-87.	11.13	139.8	83.2	5	4.5
234	123-2-87.	11.22	166	82.1	8.9	7.2
235	125-3-87.	11.26	180.1	126	14.2	10.4
236	131-4-87.	11.04	137.4	92.6	2.5	2.6
237	128-1-88.	11.05	141.1	92	1.4	2.2
238	130-2-88.	11	144.7	81.5	1.8	2.3
239	122-1-89.	11.16	136.8	86.4	2.5	2.2
240	124-2-89.	11.09	150.3	131	3	3
241	126-3-89.	11.07	132	76.2	1.6	2.4
242	132-4-89.	11.02	145	105	2.3	2.1
243	127-1-90.	11.01	122.1	81.1	2.5	2.3
244	129-2-90.	10.99	139.3	94.9	2.5	3.1
245	133-1-91.	11.08	128.9	77.1	3.4	3.6
246	137-2-91.	11.15	136.4	84.3	4.6	4.7
247	139-1-92.	10.97	132.6	98.1	2	2
248	141-2-92.	11	128.3	98.3	0.4	2.6
249	140-1-93.	10.94	135.9	100	2.1	1.8
250	142-2-93.	10.96	134	123	0	1.2
251	131-1-94.	11.23	154.1	101	3.4	3.3
252	136-2-94.	11.18	149.2	102	2	2.5
253	138-3-94.	11.21	131.2	102	1.6	2.8
254	144-4-94.	10.98	127	88.2	1.4	1.3
255	169-1-95.	10.99	102.4	69.8	1.1	2.1
256	170-2-95.	11.07	127.5	67.9	13.8	7.2
257	171-1-96.	11.12	171.4	82.7	21.4	13
258	172-2-96.	11.14	175.3	75.1	11	10.7
259	200-1-97.	11.11	162.8	91.5	8.8	8.3
260	201-2-97.	11.11	153.8	69.4	12	9.5
261	199-1-98.	11.02	122.5	94.2	3.3	4.3
262	203-2-98.	11.07	151.7	78.9	8.5	6.9
263	177-1-99.	10.99	122.2	111	5.6	5.7
264	178-2-99.	11.12	132.5	68.8	8.4	4.9
265	179-1-100.	11.12	148.9	87.1	12.5	9.3
266	181-2-100.	11.14	144.4	113	10	8.3
267	197-1-101.	11.01	142.2	104	2.1	1.8

	Sample	Dia.	M.Stress	0.2%P.S.	δ Area	δ Length
	#	mm	MPa	MPa	%	%
268	198-2-101.	10.92	142.4	105	2.1	1.9
269	185-1-102.	11.02	162.9	120	5.2	4.1
270	186-2-102.	11	163.6	118	4.3	4.3
271	14-1-103.	11.06	178.7	133	10.9	9.8
272	18-2-103.	11.26	166.9	110	9.4	7.2
273	16-1-104.	11.21	165	121	5.9	6.5
274	22-2-104.	10.95	154.9	131	4.4	3.6
275	57-1-105.	10.9	138.5	108	5.8	3.2
276	58-2-105.	10.98	152.2	105	3.1	3.3
277	52-1-106.	10.87	152.2	123	6.7	5.6
278	70-2-106.	10.94	150.7	113	2.5	2.9
279	25-1-107.	11.02	164.4	97.6	15.5	13.3
280	31-2-107.	11.03	159.2	117	7.1	6.4
281	50-1-108.	11.07	162.9	88.5	11.6	9
282	58-2-108.	10.89	147.8	109	0.2	3.6
283	57-1-109.	10.89	122.9	89.5	3.6	3.8
284	71-2-109.	11.03	135.5	111	3.1	2.9
285	91-1-110.	10.99	139.6	76.1	3.8	4
286	93-2-110.	10.99	158.1	88.3	5.7	5.2
287	173-1-111.	11.17	166.7	103	21.3	12.8
288	174-2-111.	10.97	160.7	141	14.2	12.4
289	182-1-112.	11.21	152.1	99.5	13.3	10.7
290	183-2-112.	11.16	153.2	73.7	13.2	9.9
291	185-1-113.	10.88	140.1	97	3.8	3.9
292	186-2-113.	11.01	155.2	123	3.4	2.3
293	175-1-114.	11.03	158.7	68.9	13.8	11.1
294	176-2-114.	11.11	152.5	84.5	7.9	9.4
295	180-1-115.	11.09	142.5	87.3	14.6	8.3
296	182-2-115.	11.07	132.5	104	5.3	5.6
297	189-1-116.	10.89	141.2	135	3.5	5.6
298	190-2-116.	11	145	129	3.6	5.5
299	192-1-117.	10.97	137.4	113	0.4	1.4
300	193-2-117.	11.01	140.7	118	1.3	2.3
301	194-1-118.	10.93	146.7	118	1.1	2.8
302	195-2-118.	11.02	120	90.8	1.3	1.6
303	197-1-119.	10.87	136.6	129	1.1	2.4
304	198-2-119.	11.08	123.2	91.6	1.4	1.7
305	154-1-120.	11.15	170.6	124	6.6	7.4
306	191-2-120.	10.98	140.4	123	2.9	3.7
307	92-1-121.	11.11	165.4	121	4.3	3.6
308	108-2-121.	11.08	154.6	99.2	2	1.9
309	103-1-122.	10.95	154.3	97.9	4.2	4.6
310	107-2-122.	11.09	150	114	3.9	3.8
311	173-1-123.	11.06	158.2	71.5	16.3	12.1
312	174-2-123.	11.14	149.7	110	11.8	11.9
313	41-1-124.	11.14	148.6	74.9	9.6	9.3
314	60-2-124.	10.89	130.6	83.3	3.3	2.6
315	195-1-125.	10.87	138.7	101	1.6	2

	Sample	Dia.	M.Stress	0.2%P.S.	δ Area	δ Length
	#	mm	MPa	MPa	%	%
316	198-2-125.	11.02	137.4	98.7	2.5	2.4
317	184-1-126.	11.15	116.3	91	0	0.9
318	189-2-126.	11.06	147.3	106	4.1	4.7
319	182-1-127.	11.02	139.3	83.3	10.1	6.6
320	183-2-127.	11.01	134.6	82	10.6	6.6
321	180-1-128.	11.13	145.5	73.2	12.9	9.3
322	164-2-128.	11.02	132.3	96.7	2.3	2.8
323	173-1-129.	11.12	164.7	111	15.2	11.9
324	146-2-129.	11.12	184.7	88.4	17.3	8.8
325	41-1-130.	10.9	151.8	71.1	12.9	10.8
326	60-2-130.	10.92	138.9	112	0.9	2.4
327	81-1-131.	11.05	159.7	113	7.6	7.1
328	288-2-131.	10.99	155.2	110	2.9	3.6
329	120-1-132.	11.11	129.9	106	3.7	2.5
330	289-2-132.	10.99	138.8	117	2.5	3.1
331	173-1-133.	11.06	163	91.6	13.9	10.2
332	153-2-133.	11.12	165.5	90.8	9.7	12
333	41-1-134.	11.11	146.9	76.2	10.7	9.3
334	60-2-134.	10.9	137.5	106	3.1	2
335	173-1-135.	11.12	138.4	96.2	10.9	12.2
336	212-2-135.	11.15	156.5	104	6.7	8.9
337	224-1-136.	11	148.5	103.6	1.4	4.4
338	227-2-136.	11.11	116	95.03	10.9	10
339	252-1-137.	10.95	162.7	93.54	3.4	3.1
340	289-2-137.	11.12	138.4	96.2	2.3	2.5
341	261-1-138.	10.97	140.7	116.5	2.2	3.2
342	264-2-138.	10.95	121.7	116.3	3.9	3.9
343	218-1-139.	11.21	141	97.8	12.3	8.8
344	233-2-139.	11.06	164	108	10.3	7.3
345	238-1-140.	11.06	144.9	106	3.1	3.2
346	240-2-140.	10.97	128.9	89.6	2.9	4.4
347	255-1-141.	10.95	129.3	104	3.6	3.7
348	258-2-141.	10.94	143.4	102	2.2	5.2
349	274-1-142.	11.23	146.9	104	5.1	6.3
350	278-2-142.	10.99	138.2	128	0.7	2.3
351	275-1-143.	10.9	125.8	116	4	4.5
352	279-2-143.	11.06	135.5	87.1	0.5	2.6
353	276-1-144.	10.95	124.1	110	2.5	3.6
354	280-2-144.	10.9	148.2	110	2.6	2.6
355	236-1-146.	11.05	135.2	83.6	4.7	4.1
356	264-2-146.	11.08	140.9	119	2.5	2.7
357	28-1-148.	11.18	154.8	109	5.6	4.3
358	60-1-149.	10.94	138.5	110	2.2	3.4
359	32-1-150.	11.1	167.1	105	5.3	5.3
360	134-1-151.	11.18	145.1	132	2.3	2.7
361	215-1-152.	10.95	130.8	118	3.6	5.2
362	221-2-152.	10.87	136.2	119	5.8	5.1
363	230-1-153.	11.16	167.6	117	8.4	9.3

	Sample	Dia.	M.Stress	0.2%P.S.	δ Area	δ Length
	#	mm	MPa	MPa	%	%
364	233-2-153.	11.02	154.1	115	10.1	8.6
365	206-1-154.	11.08	164.6	128	13.2	10.1
366	258-2-154.	10.88	130.5	99.3	3.3	4.3
367	240-1-154.	11.13	131.4	113	3.2	4.6
368	209-1-155.	11.12	130	118	5.3	4.6
369	274-1-155.	11.18	123.6	114	3.7	2.9
370	278-2-155.	11.08	133.9	130	0.5	2.5
371	275-1-156.	10.96	124	112	2.9	3.1
372	221-1-156.	10.95	116.8	110	0.2	2.6
373	279-2-156.	11.06	129.8	118	2.1	1.6
374	233-1-157.	10.09	159.9	99.2	12.2	10.1
375	258-1-158.	10.92	119	114	1.3	2.6
376	264-1-159.	11.02	129	109.7	4.8	2.9
377	275-1-160.	11.18	131.1	64.1	2.5	4.3
378	279-1-161.	10.95	136.3	82.4	3.8	2.7
379	292-1-162.	10.88	131.5	88.8	1.5	2.8
380	289-1-163.	10.92	136.3	88.3	2.4	2.6
381	293-1-164.	10.88	140.2	85.6	2	3
382	278-1-165.	10.95	136.7	87.9	2.7	2.3
383	291-1-166.	10.98	136.8	77.2	4	3.2
384	283-1-167.	11.04	111.9	77.3	2.5	1.3
385	169-1-168.	11.07	112.2	72.1	1.4	2.3
386	233-1-169.	11.14	152	75.3	10.5	9.2
387	258-1-170.	11.11	146.9	70.02	9.7	6.1
388	277-1-171.	11.05	127.6	80.59	3.2	5
389	269-1-172.	11.15	133.5	63.6	7.2	5
390	269-1-173.	10.93	110.5	81.97	0.5	2.9
391	282-1-174.	10.89	130	83.9	3.1	3.8
392	205-1-175.	11.14	158.7	87.2	11.2	12
393	278-1-176.	10.85	133.5	110.2	1.5	2.2
394	169-1-177.	10.98	115.7	97.09	1.5	2.5
395	207-1-178.	11.15	157.6	70.5	12.3	11.4
396	208-1-179.	11.07	114.7	97.7	2.2	4.5
397	211-1-180.	11.18	168.9	77.96	9.1	8.6
398	214-1-181.	11.11	124.8	91.9	3.4	4.6
399	217-1-182.	11.15	161.5	88.42	6.7	7
400	220-1-183.	10.8	114.7	75.2	1.8	3.1
401	225-1-184.	10.94	110.3	66.82	0	2.2
402	207-1-185.	11.1	148.9	70.5	11.5	10.5
403	211-1-186.	11.22	168.3	92.3	9.7	9.9
404	214-1-187.	10.93	112.4	104.6	0.7	2
405	233-1-188.	10.96	109.4	88.19	2.4	2.5
406	226-1-189.	11.21	166.8	90.15	9.4	7.3
407	229-1-190.	11.17	163.3	80.53	9.8	9.1
408	232-1-191.	11.13	151.4	104	7.2	7.9
409	235-1-192.	10.97	121.6	93.78	1.8	2.3
410	239-1-193.	10.91	123	70.27	0.7	1.5
411	251-1-194.	11.06	115.4	73.44	2.2	1.9

	Sample	Dia.	M.Stress	0.2%P.S.	δ Area	δ Length
	#	mm	MPa	MPa	%	%
412	254-1-195.	10.96	117.2	100.8	1.3	1.6
413	257-1-196.	10.88	121.2	71.49	1.6	2.4
414	263-1-197.	10.86	125.3	78.32	1.8	1.8
415	267-1-198.	11.05	120.9	86.88	1.2	1.7
416	273-1-199.	11.03	129.1	88.59	4.7	1.9
417	260-1-200.	10.92	115.7	89.54	2	1.6
418	233-1-201.	10.93	163.6	87.15	3.1	9.3
419	213-1-202.	11.23	153.8	101.9	3.7	6.3
420	216-1-203.	11.05	129.9	104.1	3.1	4.9
421	285-1-204.	11.13	141.7	74.91	6.7	3.4
422	270-1-205.	10.95	136.2	123.3	1.6	3
423	271-1-206.	10.94	128.2	113.2	2.2	0.9
424	207-1-207.	11.17	155	62.4	10.8	8.5
425	210-1-208.	11.04	131.8	58.8	7.6	6.9
426	233-1-209.	11.06	151.9	115.2	2	6.7
427	239-1-210.	10.87	118.4	105	2.2	2.4
428	251-1-211.	11.07	123.1	97.86	0.9	3.3
429	260-1-212.	10.98	119.5	91.6	1.3	2.7
430	267-1-213.	11.07	113.2	87.86	2	1.8
431	269-1-214.	11.06	118.4	69.97	1.6	3.2
432	275-1-215.	11.05	133.6	70.86	3.4	3.8
433	289-1-216.	11.05	149.1	76.7	1.3	2.5
434	207-1-217.	11.04	152.6	63.15	9	9.3
435	210-1-218.	11.09	133.2	70.2	6.9	6.5
436	272-1-219.	11.01	129.9	105.5	0.7	1.4
437	240-1-220.	11.07	114.5	87.95	3	2
438	258-1-221.	11.1	149.9	100.3	9	6.5
439	213-1-222.	11.15	163.8	83.5	11	9.3

	Sample	Dia.	M.Stress	0.2%P.S.	δ Area	δ Length
	#	mm	MPa	MPa	%	%
440	219-1-223.	11.17	140.7	116.6	5.1	5.7
441	222-1-224.	11.13	164.7	90.88	9.1	7.2
442	225-1-225.	10.97	108.9	97.06	5.5	3.9
443	228-1-226.	11.17	148.6	105.6	2.7	5.4
444	233-1-227.	11.17	158.3	100.7	10.1	9.3
445	234-1-228.	11.11	160.2	116.8	8.5	6.6
446	231-1-229.	11.08	166.6	88.22	9.2	9.5
447	237-1-230.	11.04	137.9	102.3	5.4	5
448	240-1-231.	11.03	131.2	82.37	3.9	3.3
449	250-1-232.	10.97	129	89.75	1.6	3.2
450	251-1-233.	10.84	115.6	88.02	0.2	2.3
451	253-1-234.	11	128.9	99.31	3.8	2
452	256-1-235.	11.1	143.6	77.18	5.3	5.3
453	289-1-236.	10.95	133.8	94.49	4	2.4
454	259-1-237.	11.19	147.9	108.5	7.2	5.1
455	260-1-238.	10.89	114.9	108.3	1.6	2.2
456	281-1-239.	10.88	137.7	80.92	2	2
457	262-1-240.	11.06	138.8	88.14	3.4	3.7
458	265-1-241.	10.93	132.4	108.3	2.7	1.7
459	277-1-242.	11.05	136.8	88.29	4.7	5.3
460	275-1-243.	10.98	136.7	113.1	4.1	4.5
461	276-1-244.	11.15	136.5	69	6.7	5.9
462	279-1-245.	10.8	148.4	106.1	3.7	3.8
463	280-1-246.	10.86	138.8	106.8	2.9	2.9
464	282-1-247.	11.15	150.6	94.01	7.6	7.2
465	284-1-248.	11.02	127.5	91.57	2.7	5
466	283-1-249.	11.16	150.2	83.61	8.1	6.7
467	286-1-250.	10.86	123.3	107.4	2.6	3

	Sample	Dia.	M.Stress	0.2%P.S.	δ Area	δ Length
	#	mm	MPa	MPa	%	%
468	287-1-251.	11.04	137	77.22	4.7	5.8
469	293-1-252.	10.91	146.2	109.9	2	3
470	291-1-253.	11.08	144.1	108.7	2	4.4
471	292-1-254.	10.9	131.6	122	1.5	2
472	234-1-255.	11.05	159.1	117.9	6.4	10.2
473	237-1-256.	11.03	115.1	111.9	2.2	2.2
474	251-1-257.	11.02	123.4	105.9	0.9	3.1
475	256-1-258.	11.04	135.8	97.05	3.9	4
476	259-1-259.	11.17	149.1	112.6	8.9	6.5
477	260-1-260.	11.02	116.1	102.3	1.4	1.4
478	281-1-261.	10.86	137.8	101.9	2.6	1.6
479	234-1-262.	11.14	161.9	93.69	5.5	9.8
480	251-1-263.	10.81	118.3	112.3	1.5	2.1
481	256-1-264.	11.1	148.1	109.1	8.5	6.6
482	259-1-265.	11.13	154.3	98.77	10.3	7.8
483	275-1-266.	11.01	146.1	128.9	6.3	6.2
484	276-1-267.	11.08	137.9	107.7	6.2	5.6
485	279-1-268.	10.78	132.6	114.1	1.5	1.5
486	294-1-269.	11.03	138.5	90.42	8	5.4
487	RM10	10.9	129	98.9	6.5	3.9
488	RM11	11	156.5	122	6.9	6.3
489	HAM1	11.1	170.2	123	17.1	14.4
490	AX65	11.21	174.2	103.2	17.5	14.1
491	RMF	11.01	148.5	140.6	5.6	6.1
492	RMG	11.05	137.14	120	2.4	4
493	RMX	10.97	138.2	97.99	3.6	3
494	RMY	10.88	142.4	101.8	4.7	5
495	RMZ	10.96	129.7	66	3.4	4.7

Appendix N

Condensed Composition, Mechanical, and Structural Analysis Results.

	SAMPLE	Silicon	Strontium	Sodium	Iron	Magnesium	Manganese	Titanium	Boron	Copper	U.T.S.	P.S.	*A	*L	Hv10	Std. Dev.	Poro	Poro	Mod.#	Std. Dev.	Grain#
	#	%	%	%	%	%	%	%	%	%	MPa	MPa	%	%	kg/mm^2	kg/mm^2	Std. No.	Area %	AFS	AFS	ASTM
	Sr																				
1	37-1-2	10.0558	0.0214	0.0004	0.1827	0.0023	0.0377	0.0056	0.0003	0.0007	139.1	90	11.5	10.5	42.8	0.7627	4.83	0.5677	4.8333	1.2583	8.05
5	61-1-3	10.0506	0.0115	0.0007	0.1475	0.0028	0.0013	0.0056	0.0003	0.0019	132.5	73.1	7.8	7.8	41	0.5007	5.67	0.9149	4	0.5	8.3
13	109-1-5	13.0668	0.0207	0.0001	0.1733	0.0042	0.0015	0.0078	0.0001	0.0007	133.2	66.1	9.3	5.6	47.9	1.2481	4.33	0.4727	4.8333	0.2887	8.4
15	97-1-6	12.9144	0.0154	0.0001	0.1808	0.004	0.0069	0.0078	0.0003	0.0017	131			3.9	47.7	0.8262	1.83	0.0415	4.5	0.5	7.8
25	180-1-9	11.3969	0.0139	0.0001	0.1563	0.0026	0.002	0.0067	0.0007	0.0007	136.9	62.4	7.9	7.5	44.7	4.3807	1.33	0.0165	3.6667	1.1547	7.05
26	181-2-9	11.2766	0.0091	0	0.1577	0.0021	0.002	0.0068	0.0002	0.0006	130	120	10	6.1	45.3	0.9852	2.17	0.0738	3	1	6.3
27	182-3-9	11.4324	0.009	0.0001	0.1586	0.0018	0.0021	0.0067	0.0002	0.0007	134.6	95	1.4	3.7	45.9	1.3761	1.17	0.0085	3.6667	1.5275	6.8
28	183-4-9	11.2132	0.0149	0	0.1588	0.0016	0.0022	0.0067	0.0002	0.0007	135	90	8	6.5	45.2	1.1077	2	0.05	3.3333	1.5275	6.3
87	109-1-31	12.933	0.0227	0.0013	0.1747	0.0027	0.0044	0.0073	0	0.0009	127.4	113.3	6.1	4.8	49.6	2.6498	1.5	0.025	3.6667	0.5774	8.3
111	37-1-39	10.3423	0.0306	0.0018	0.1428	0.0023	0.0033	0.0055	0	0.0006	135.4	99	11.9	9.5	42.7	1.2356	1	0	4.6667	1.0408	7.55
255	169-1-95	11.8009	0.0002	0.0017	0.1688	0.0019	0.003	0.0108	0	0.003	102.4	69.84	1.1	2.1	49.4	1.9799	1	0	1	0	6.45
263	177-1-99	11.7324	0.0048	0.0009	0.1665	0.0015	0.0029	0.0102	0	0.0029	122.2	110.7	5.6	5.7	47.3	0.7118	1	0	2.3333	1.893	5.8
264	178-2-99	11.9014	0.0093	0.0007	0.1678	0.0017	0.0037	0.0102	0	0.0031	132.5	68.78	8.4	4.9	46.3	0.3987	1	0	3.5	1.8028	7.8
265	179-1-100	11.7048	0.0195	0.0006	0.1633	0.0015	0.0028	0.0099	0	0.0029	148.9	87.07	12.5	9.3	47	1.5587	1.33	0.0165	4.6667	0.5774	8.3
266	181-2-100	11.9848	0.0284	0.0006	0.1636	0.0012	0.0035	0.0099	0	0.0029	144.4	113	10	8.3	45.4	1.4846	1	0	3.6667	0.5774	6.8
289	182-1-112	11.9325	0.0279	0.0005	0.1665	0.001	0.0029	0.0101	0	0.003	152.1	99.54	13.3	10.7	46.4	0.5428	2.67	0.1438	4.8333	0.2887	6.3
290	183-2-112	12.1913	0.0352	0.0004	0.1658	0.0009	0.0036	0.0103	0	0.0031	153.2	73.66	13.2	9.9	46.5	0.9988	1	0	4.5	0.5	6.8
295	180-1-115	11.6641	0.0305	0.0001	0.1731	0.0027	0.0068	0.012	0	0.0028	142.5	87.33	14.6	8.3	44.7	0.5419	3.33	0.2626	4.5	0.866	7.8
296	182-2-115	11.4903	0.0683	0.0002	0.1741	0.0029	0.008	0.0118	0	0.0029	132.5	104.2	5.3	5.6	45.8	0.8091	4.17	0.4423	4.6667	1.4434	7.55
319	182-1-127	11.8146	0.0366	0.0003	0.1648	0.0006	0.0028	0.0103	0	0.0029	139.3	83.34	10.1	6.6	47.2	0.814	1	0	4.6667	0.5774	7.55
320	183-2-127	11.7212	0.0476	0.0003	0.1666	0.0005	0.0036	0.0101	0	0.0029	134.6	81.99	10.6	6.6	48.7	0.9948	1.83	0.0415	4.1667	1.0408	7.05
321	180-1-128	11.7682	0.024	0.0003	0.1664	0.0007	0.0028	0.0102	0	0.0029	145.5	73.16	12.9	9.3	47.2	1.0534	1	0	4.1667	1.0408	6.8
	No Mod.																				
17	169-1-7	11.2698	0	0.0001	0.1563	0.0022	0.0014	0.0066	0.0002	0.0006	109	70			46	0.6274	1.17	0.0085	0.5	0	7.8
	Na																				
9	1-1-4	9.9834	0	0.0155	0.1402	0.0024	0.0044	0.0054	0.0003	0.0007	149	70	8	10.2	45.3	0.3204	4.33	0.4727	6	0	7.3
18	170-2-7	11.3021	0	0.0032	0.1572	0.0012	0.0016	0.0066	0.0044	0.0007				4.6	46.9	1.3126	1.17	0.0085	1.6667	0.5774	7.3
19	171-3-7	11.645	0	0.0034	0.1579	0.0005	0.0018	0.0067	0.0002	0.0007	128.2	87	8.7	8.5	48.3	0.8313	1.17	0.0085	1.6667	0.2887	7.3
20	172-4-7	11.3333	0	0.0116	0.1578	0.0003	0.0019	0.0065	0.0002	0.0007	165.1	68.5	18.1	11.7	46.6	0.2858	4.17	0.4423	5.3333	0.5774	7.05
31	1-1-11	9.7779	0	0.0066	0.1497	0.0004	0.0009	0.0058	0.0001	0.0004	145.6	87	18.7	11.8	49.2	1.9229	1	0	3.5	0.866	7.55
43	37-1-15	9.5434	0	0.0003	0.1458	0.0025	0.0014	0.0057	0.0001	0.0003	105.3	82	10.3	7.5	46.4	0.8085	1	0	1	0	6.8
55	73-1-19	12.6893	0.0003	0.0141	0.173	0.0028	0.0017	0.0076	0	0.0006	167.2	128	17.6	12.6	50	1.4029	1.5	0.025	4.5	0.5	8.3
95	1-1-33	10.2344	0.0003	0.0132	0.1427	0.0024	0.0043	0.0053	0	0.0006	153.2	116	20.6	12.9	46.3	0.8832	2	0.05	5	0.5774	7.05
256	170-2-95	11.7463	0.0002	0.003	0.1702	0.0015	0.0037	0.0103	0	0.0033	127.5	67.85	13.8	7.2	51.6	0.6145	1	0	1.8333	0.2887	6.8
257	171-1-96	11.4638	0.0003	0.009	0.1621	0.0011	0.0028	0.0092	0	0.0024	171.4	82.72	21.4	13	50.7	1.7475	1.5	0.025	4	0.5	6.3
258	172-2-96	11.6145	0.0003	0.0098	0.1665	0.0015	0.0038	0.0093	0	0.0027	175.3	75.14	11	10.7	47.8	2.3037	1.17	0.0085	3.6667	1.893	7.05
287	173-1-111	11.9623	0.0005	0.0106	0.164	0.001	0.0027	0.01	0	0.003	166.7	102.6	21.3	12.8	50.2	0.9778	1	0	3.6667	2.3094	7.3
288	174-2-111	11.9819	0.0003	0.0174	0.1638	0.0003	0.0033	0.0099	0	0.0032	160.7	141.1	14.2	12.4	48.1	1.1856	1.33	0.0165	5.8333	1.6073	7.55
293	175-1-114	11.7434	0.0001	0.0386	0.1612	0.0007	0.0027	0.0098	0	0.003	158.7	68.86	13.8	11.1	48.2	1.0178	2.17	0.0738	7.5	0.5	7.8
294	176-2-114	11.6654	0.0002	0.0534	0.1577	0	0.0033	0.0094	0	0.0032	152.48	84.48	7.9	9.4	48.3	0.3266	4.33	0.4727	7.6667	0.5774	8.9

	SAMPLE	Silicon	Strontium	Sodium	Iron	Magnesium	Manganese	Titanium	Boron	Copper	U.T.S.	P.S.	*A	*L	Hv10	Std. Dev.	Poro	Poro	Mod.#	Std. Dev.	Grain#
	#	%	%	%	%	%	%	%	%	%	MPa	MPa	%	%	kg/mm^2	kg/mm^2	Std. No.	Area %	AFS	AFS	ASTM
311	173-1-123	11.863	0	0.0272	0.1644	0.0013	0.0044	0.0105	0	0.003	158.2	71.5	16.3	12.1	48.1	1.3018	2	0.05	7.5	0.5	8.55
312	174-2-123	11.7188	0	0.0379	0.1608	0.0008	0.0052	0.0103	0	0.0031	149.7	109.8	11.8	11.9	47.1	2.2474	4.83	0.5677	7.6667	0.5774	9.3
323	173-1-129.	11.7177	0.0004	0.0115	0.1681	0.0007	0.0041	0.011	0	0.0029	164.7	111	15.2	11.9	50.2	1.8085	1	0	5.3333	1.5275	7.55
331	173-1-133	11.7006	0	0.0071	0.1711	0.0019	0.0076	0.0108	0	0.0029	163	91.59	13.9	10.2	50.5	1.3049	4.5	0.505	4.1667	0.2887	7.05
335	173-1-135	11.618	0	0.0177	0.1617	0.0013	0.0045	0.0111	0	0.0027	156.5	104	10.9	12.2	48.8	1.5497	5.17	0.6799	7	0	9.15
445	234-1-228.	12.8912	0.0008	0.033	0.2894	0.001	0.0069	0.0099	0.0001	0.0018	160.2	116.8	8.5	6.6	53.6	2.5618	1.67	0.0335	6.3333	1.4434	8.8
	Mg Sr																				
2	43-2-2	9.983	0.0133	0.0003	0.1813	0.1201	0.0379	0.0053	0.0003	0.0007					50.5	1.1161	6	1.07	4.3333	0.5774	8.05
6	67-2-3	9.9713	0.0048	0.0001	0.1447	0.0845	0.0011	0.0054	0.0003	0.0021	124.4	102.8	3.3	4.7	50.7	0.5797	3.67	0.3374	1.5	0.5	6.8
44	43-2-15	9.7005	0.0032	0.0005	0.1458	0.0649	0.0018	0.0056	0.0003	0.0004	121	87.4	3.5	4.1	48	0.9606	1.5	0.025	1.5	0	7.8
88	115-2-31	13.0546	0.0246	0.0021	0.1733	0.0942	0.0045	0.0074	0	0.011	125.4	84.3	3.4	4.1	51	2.2295	1.83	0.0415	2.8333	0.2887	7.8
115	43-1-40	10.3562	0.0219	0.0027	0.1393	0.0979	0.0031	0.0055	0	0.0006	127	78.9	4.8	4.9	49.3	0.5292	2	0.05	4	1	8.55
	Mg Na																				
10	7-2-4	10.0453	0	0.0228	0.1352	0.0537	0.0046	0.0051	0.0002	0.0007	149.5	105	10.7	12.8	46.8	0.9347	5.5	0.835	6	0	8.8
32	7-2-11	9.7839	0	0.0071	0.1544	0.0797	0.0012	0.0053	0.0003	0.0004	141.4	85.56	7	6.6	48.5	1.949	1	0	3.1667	0.7638	6.55
56	79-2-19	12.9329	0.0002	0.0117	0.1838	0.078	0.0023	0.0077	0	0.0007	138.6	128	5.9	3.5	51.3	1.1669	1.17	0.0085	4.3333	0.5774	8.3
75	79-1-26	13.4957	0	0.0106	0.1744	0.0983	0.0038	0.0079	0	0.0012	138.6	75.22	3.7	3.5	53.3	1.4095	3.67	0.3374	4	0	9.05
101	7-1-35	10.2219	0.0008	0.0197	0.1363	0.1041	0.0034	0.0055	0	0.0006	143.1	98.3	7.5	8.1	48.4	1.0469	5	0.6	5	0	7.3
125	79-1-44	12.5219	0.0006	0.0177	0.1635	0.0963	0.0046	0.0068	0	0.0008	143.1	96	4.9	6.7	51.6	0.8954	3	0.19	4	0	8.55
	Mn Sr																				
83	157-1-29	11.5754	0.0269	0.0023	0.157	0.0052	0.2098	0.0063	0	0.0007	143.8	61.13	15.5	9.4	48.2	0.4604	2	0.05	4	1.7321	7.55
84	160-2-29	11.5265	0.0205	0.0029	0.1615	0.0046	0.2099	0.0064	0	0.0007	145.9	84	15	8.8	49.7	0.9201	1.67	0.0335	3.6667	1.5275	7.8
112	39-2-39	10.2715	0.0263	0.0026	0.1448	0.0024	0.2299	0.0055	0	0.0006	144	95	12.4	10.7	45.5	0.5128	1	0	4.6667	1.5275	8.05
113	41-3-39	10.1985	0.0251	0.0025	0.1466	0.0021	0.5556	0.0054	0	0.0006					47	1.2596	2	0.05	4.3333	1.5275	8.3
135	111-1-48	12.9113	0.0275	0.0016	0.1729	0.0028	0.1928	0.0075	0	0.0009	131.5	77.6	7	6	49	1.8447	1.17	0.0085	4.1667	1.7559	8.05
136	113-2-48	12.9819	0.024	0.0017	0.1786	0.0018	0.4814	0.0075	0	0.001	140.5	87.1	8.6	6.8	52	2.3269	1.17	0.0085	4.5	1.3229	7.7
313	41-1-124	10.6683	0.0303	0.0003	0.1622	0.0023	0.5396	0.0085	0	0.003	148.6	74.91	9.6	9.3	48	1.2172	6	1.07	4.3333	1.1547	6.8
325	41-1-130	10.393	0.0242	0.0007	0.156	0.0004	0.2314	0.0091	0	0.0026	151.8	71.14	12.9	10.8	46.9	1.4049	1	0	4.3333	1.1547	8.55
333	41-1-134	10.3373	0.0305	0.0001	0.1566	0.0017	0.555	0.0085	0	0.0031	146.9	76.23	10.7	9.3	48.9	0.7223	4	0.41	4.8333	0.2887	7.05
	Mn No Mod.																				
40	5-2-13	9.8561	0	0.0008	0.2112	0.0001	0.5894	0.006	0.0004	0.0005	123.5	92.3	3.2	5.7	49.6	1.4593	1	0	1	0	7.3
51	39-1-17	9.7182	0.0006	0.0018	0.1401	0.0024	0.1835	0.0057	0.0003	0.0003	121.4	58.11	8	5.9	45.1	0.725	1.17	0.0085	1.3333	0.2887	7.3
52	41-2-17	10.103	0.0001	0.0017	0.147	0.0018	0.4752	0.0059	0.0006	0.0005	119.5	66	4.9	5.9	50.6	0.4416	1	0	1.1667	0.2887	8.05
	Mn Na																				
39	3-1-13	9.707	0	0.003	0.1723	0.0007	0.2012	0.0056	0.0003	0.0004	124.2	72.4	7.6	7.7	49	1.6096	1.33	0.0165	1.6667	0.2887	7.05
63	75-1-21	12.5905	0	0.0037	0.1924	0.0021	0.1647	0.0076	0.0001	0.0006	122.5	120	6.5	5.9	51.4	1.5895	1.17	0.0085	2.3333	1.1547	8.4
64	77-2-21	13.0724	0	0.0028	0.2147	0.0017	0.4398	0.008	0.0004	0.0008	122.6	92.5	6.6	3.6	51.6	1.0265	1	0	1.3333	0.5774	8.9
85	77-1-30	12.9444	0.0005	0.01	0.1729	0.0019	0.4669	0.0071	0	0.0009	172.4	76.9	10.8	10.7	52	0.5992	1	0	3.8333	1.0408	7.8
99	3-1-34	10.1833	0.0002	0.0121	0.1412	0.0013	0.1939	0.0054	0	0.0006	156.9	98.92	12.3	9.6	46.8	0.8824	2.83	0.1662	5.6667	0.5774	7.8
100	5-2-34	10.165	0.0003	0.0107	0.1441	0.0006	0.4775	0.0053	0	0.0006	166.1	119.6	19.6	12.3	47.3	0.9647	1.17	0.0085	5.3333	0.5774	7.05
123	75-1-43	12.6672	0.0009	0.0208	0.1634	0.0024	0.1964	0.0067	0	0.0008	155.6	96.5	12.2	10.3	53.1	1.5306	1.33	0.0165	6	1	7.8
139	145-1-50	11.4191	0.0006	0.0173	0.1498	0.0022	0.165	0.0062	0	0.0007	157.9	68.8	12.8	12.1	47.8	2.2287	2.83	0.1662	5.6667	1.1547	9.3
	Fe Sr																				
67	110-1-23	12.6032	0.0084	0.0023	0.6639	0.0033	0.0027	0.008	0.0002	0.0007	161.3	101.2	4.9	4.8	53.1	3.5758	1.5	0.025	3.6667	1.5275	9.4
91	38-1-32	10.0201	0.0206	0.0002	0.6152	0.0035	0.0019	0.0053	0	0.0008	153.1	84.9	9.3	8.4	46	1.2707	1.83	0.0415	4.5	0.5	7.3

	SAMPLE	Silicon	Strontium	Sodium	Iron	Magnesium	Manganese	Titanium	Boron	Copper	U.T.S.	P.S.	*A	*L	Hv10	Std. Dev.	Poro	Poro	Mod.#	Std. Dev.	Grain#
	#	%	%	%	%	%	%	%	%	%	MPa	MPa	%	%	kg/mm^2	kg/mm^2	Std. No.	Area %	AFS	AFS	ASTM
131	110-1-47	12.6595	0.0276	0.0017	0.6121	0.0028	0.0045	0.0075	0	0.0011	119.4	85.8	3	3	51.9	1.8826	1.17	0.0085	4	1.7321	8.2
251	131-1-94	12.8411	0.0288	0.0006	0.714	0.0035	0.008	0.0373	0	0.0038	154.1	101.3	3.4	3.3	53.9	1.4662	1	0	5.1667	1.0408	8.2
	Fe No Mod.																				
47	38-1-16	9.4455	0.0005	0.0006	0.6107	0.0039	0.0023	0.0057	0.0003	0.0006	112.9	98	3.5	4.6	48.7	1.3819	1	0	1	0	8.3
	Fe Na																				
35	2-1-12	9.5065	0	0.0076	0.6212	0.0011	0.0038	0.0055	0.0003	0.0007	151.2	98.9	7.8	5.5	52.6	2.9951	1	0	4.1667	0.2887	7.3
59	74-1-20	12.5952	0	0.0112	0.6712	0.0037	0.0029	0.0079	0.0004	0.0007	179.1	123	6.5	6.8	55.6	1.0439	1	0	3.5	0.5	8.3
96	2-2-33	10.2606	0.0004	0.0192	0.62	0.0017	0.005	0.0052	0.0081	0.0008	164	119	8.6	9.8	48.8	0.582	4	0.41	6	0	8.55
119	74-1-42	13.1678	0.0006	0.0131	0.5925	0.0024	0.0041	0.0071	0.0077	0.0011	168.2	105.2	7.5	7.9	54.2	2.0724	4.17	0.4423	4.3333	0.5774	8.3
	Ti Sr																				
29	204-1-10	11.5124	0.0045	0	0.1581	0.0026	0.0013	0.1155	0.0001	0.0007	118	82	1.4	3.6	48.7	0.9988	2.67	0.1438	1.6667	0.2887	7.95
30	205-2-10	11.3194	0	0	0.1574	0.0021	0.0014	0.2349	0	0.0008	125.6	65	4.4	4.1	50.1	1.5052	1.67	0.0335	1.6667	0.2887	12.55
187	49-1-72	9.7356	0.0294	0.0008	0.1347	0.002	0.0044	0.1013	0	0.0005	141.3	72.11	12.6	8	44.9	0.1835	1.83	0.0415	4.3333	1.1547	8.55
199	61-1-76	10.2681	0.028	0.0011	0.1492	0.0016	0.0027	0.1944	0	0.0025	144.1	70.73	10.8	8.6	45.7	0.6713	2.83	0.1662	4	1.3229	12.9
233	121-1-87	13.2051	0.0268	0.0008	0.1713	0.0025	0.006	0.1086	0	0.0034	139.8	83.15	5	4.5	52.1	2.0285	1	0	4.3333	0.2887	8.9
245	133-1-91	13.0293	0.0232	0.0002	0.1799	0.0017	0.0061	0.1979	0	0.0037	128.9	77.14	3.4	3.6	50.5	1.2384	1	0	4	1	12.15
262	203-2-98	11.5348	0.0358	0.0006	0.163	0.001	0.0036	0.1087	0	0.0026	151.7	78.9	8.5	6.9	48.5	0.5164	1.17	0.0085	4.1667	1.0408	8.3
	Ti No Mod.																				
261	199-1-98	11.2976	0	0.0007	0.1615	0.0011	0.0028	0.1108	0	0.0025	122.5	94.15	3.3	4.3	48.9	0.7083	1.17	0.0085	1.1667	0.2887	10.3
385	169-1-168	12.0082	0	0.0001	0.2697	0.0016	0.0082	0.0095	0	0.0029	112.2	72.1	1.4	2.3	50.1	1.5921	4	0.41	1	0	8.3
394	169-1-177.	10.9723	0	0.0001	0.2753	0.0014	0.0095	0.0108	0	0.0022	115.7	97.09	1.5	2.5	48.2	0.6555	4.83	0.5677	1	0	7.8
	Ti Na																				
155	13-1-58	10.0445	0	0.0209	0.1427	0.0039	0.002	0.096	0.0001	0.0007	153.7	98.9	13.7	13.3	47.2	0.367	1	0	6.3333	0.5774	8.8
183	25-1-70	9.8298	0	0.0128	0.1347	0.0013	0.0029	0.0945	0	0.0005	159.6	89.63	15.7	12.6	46.7	0.5845	1.5	0.025	4.8333	0.7638	9.3
209	85-1-79	13.0447	0	0.0162	0.1752	0.0011	0.0063	0.1023	0	0.0037	168.3	82.33	12.1	8.5	55.1	1.0857	1	0	5.8333	1.0408	9.3
221	97-1-83	13.2016	0.0006	0.0172	0.1728	0.0027	0.0063	0.1943	0	0.0037	166.3	77.4	14.1	11.3	52.2	0.9475	3	0.19	7.3333	0.5774	11.4
259	200-1-97	11.5741	0.0002	0.005	0.1628	0.001	0.0028	0.1051	0	0.0026	162.8	91.52	8.8	8.3	52	1.524	1	0	3.5	0.5	9.3
260	201-2-97	11.7812	0.0006	0.0336	0.1572	0.0003	0.0034	0.0994	0	0.0028	153.8	69.4	12	9.5	49.5	1.2372	1.83	0.0415	6.5	0.5	9.8
279	25-1-107	10.711	0.0002	0.0143	0.1497	0.0018	0.0037	0.1913	0	0.0028	164.4	97.63	15.5	13.3	48.3	0.8681	1.83	0.0415	6.3333	0.5774	13.4
489	HAM1	12.849	0	0.0129	0.1059	0.0009	0.0023	0.0146	0.0001	0.0009	170.2	123	17.1	14.4	52	1.6444	1	0	6.1667	0.5774	9.7
490	AX65	12.7455	0	0.012	0.1176	0.0009	0.0021	0.0256	0.0002	0.0054	174.2	103.2	17.5	14.1	50.1	1.0733	1	0	5.6667	1.1547	9.9
	B Sr																				
384	283-1-167.	11.9536	0.0081	0.0005	0.2428	0.0015	0.0049	0.0048	0.0232	0.0054	111.9	77.3	2.5	1.3	49.6	1.2377	5.17	0.6799	2	0	12.65
389	269-1-172.	12.1705	0.0214	0.0001	0.2835	0.0016	0.0035	0.0079	0.0051	0.0017	133.5	63.6	7.2	5	47.9	1.7002	5	0.6	4.1667	1.0408	8.3
396	208-1-179.	9.9325	0.0167	0.0001	0.2367	0.0015	0.0035	0.0001	0.0416	0.0015	114.7	97.7	2.2	4.5	47.2	1.1713	6	1.07	1.1667	0.2887	12.4
400	220-1-183.	12.4324	0.0154	0	0.2571	0.0033	0.0102	0.0007	0.0404	0.0025	114.7	75.2	1.8	3.1	52	2.567	1.83	0.0415	2.3333	0.2887	11.55
404	214-1-187.	11.3839	0.0174	0.0001	0.2883	0.0012	0.0037	0.0031	0.0457	0.0012	112.4	104.6	0.7	2	48.8	0.9737	6	1.07	1	0	12.9
410	239-1-193.	11.6571	0.0304	0.0001	0.2855	0.0019	0.0036	0.0065	0.0569	0.0117	123	70.27	0.7	1.5	49.1	1.0986	1.5	0.025	1.3333	0.2887	13.15
431	269-1-214.	11.4365	0.0194	0.0001	0.2903	0.0017	0.0044	0.0039	0.0568	0.0011	118.4	69.97	1.6	3.2	49.3	3.2948	1.5	0.025	1.6667	0.5774	13.4
	B No Mod.																				
405	233-1-188.	11.7044	0.0003	0.0001	0.2521	0.0017	0.0035	0.0048	0.0492	0.0013	109.4	88.19	2.4	2.5	50	1.2818	5.67	0.9149	1	0	11.4
	B Na																				
392	205-1-175.	10.2075	0.0001	0.0195	0.2474	0.0009	0.0042	0.0009	0.0354	0.0026	158.7	87.2	11.2	12	46.5	1.314	3.5	0.3	5.8333	1.0408	13.65
399	217-1-182.	12.4841	0.0002	0.0095	0.2532	0.002	0.0097	0.0009	0.0318	0.0027	161.5	88.42	6.7	7	52.8	2.0967	3	0.19	5	0	13.4
406	226-1-189.	11.9533	0	0.0083	0.2499	0.0011	0.0036	0.0006	0.0442	0.0011	166.8	90.15	9.4	7.3	51.2	1.9894	3.83	0.3726	4.5	0.866	13.4

	SAMPLE	Silicon	Strontium	Sodium	Iron	Magnesium	Manganese	Titanium	Boron	Copper	U.T.S.	P.S.	*A	*L	Hv10	Std. Dev.	Poro	Poro	Mod.#	Std. Dev.	Grain#
	#	%	%	%	%	%	%	%	%	%	MPa	MPa	%	%	kg/mm^2	kg/mm^2	Std. No.	Area %	AFS	AFS	ASTM
407	229-1-190.	11.9544	0	0.013	0.2907	0.0006	0.0036	0.001	0.0392	0.0013	163.3	80.53	9.8	9.1	52.8	2.006	1.5	0.025	4.8333	0.7638	11.9
408	232-1-191.	11.9454	0	0.0354	0.2562	0.0005	0.003	0.0045	0.0661	0.0011	151.4	104	7.2	7.9	50.2	1.2271	3.67	0.3374	7.3333	0.5774	13.4
	Mn Mg Sr																				
45	45-3-15	9.9403	0.0017	0.0007	0.1564	0.0514	0.1831	0.0058	0.0001	0.0005	119.4	90.58	6.3	6	51.3	1.9604	1.17	0.0085	1	0	5.55
79	159-1-27	11.7643	0.0191	0.003	0.1569	0.0965	0.2074	0.0066	0	0.0008	140.7	85.86	6.3	4.9	49.1	0.9416	1.5	0.025	4	1.7321	7.3
89	117-3-31	13.0959	0.0263	0.0026	0.1823	0.1006	0.1833	0.0074	0	0.001	127.7	66.8	3.5	5	52.7	2.0253	1.17	0.0085	3.1667	1.0408	8.3
90	120-4-31	13.2472	0.0216	0.0025	0.189	0.11	0.3876	0.0075	0	0.0011	139.5	122	3.7	4.5	55.4	2.8722	2.83	0.1662	3.6667	0.5774	7.8
117	45-1-41	10.2699	0.0261	0.003	0.1396	0.0983	0.1699	0.0055	0	0.0008	127.1	80.7	5.3	5.7	49.5	1.1361	2.17	0.0738	4.3333	0.5774	7.8
118	47-2-41	10.3067	0.0191	0.0038	0.1466	0.0942	0.4739	0.0054	0	0.0006	161.1	95.8	7.8	8	53.2	1.507	2.5	0.12	4.6667	1.5275	6.05
	Mn Mg No Mod.																				
46	47-4-15	10.3121	0	0.0008	0.1633	0.0217	0.474	0.006	0.0003	0.0005	123.5	82	3.6	4.7	50.3	1.6726	1	0	1.3333	0.2887	5.55
	Mn Mg Na																				
33	9-3-11	10.0666	0	0.0035	0.2	0.0549	0.2445	0.0055	0.0002	0.0004	133.2	63.09	10.3	7.3	48.8	1.3615	1	0	1.5	0	6.3
34	11-4-11	10.379	0	0.0045	0.2231	0.0373	0.6155	0.0056	0	0.0006	126.7	94.2	5.2	6.5	49.6	0.6099	1	0	1.8333	1.0408	7.3
57	81-3-19	13.1926	0	0.0057	0.1847	0.0544	0.2005	0.0081	0.0001	0.0007	131.4	118	11.2	8.6	49.6	1.0304	1	0	2.6667	0.2887	8.8
58	83-4-19	13.6003	0	0.0104	0.1906	0.0431	0.4901	0.0083	0.0002	0.0009					54.1	2.1018	1.17	0.0085	3.3333	0.5774	7.8
76	81-2-26	13.5446	0	0.0078	0.1819	0.086	0.2114	0.008	0	0.0013	149.7	79.89	4.9	4.5	52.8	3.4117	2.83	0.1662	2.6667	0.5774	8.3
77	83-3-26	13.708	0	0.0083	0.185	0.0887	0.4874	0.0081	0	0.0014	145.8	91.03	3.4	3	54.4	3.0971	4.83	0.5677	2.5	0.5	8.2
102	9-2-35	10.3366	0.001	0.0214	0.1386	0.1035	0.2102	0.0055	0	0.0007	147.2	103.9	9	7.4	51.1	1.2388	2.67	0.1438	5.3333	0.5774	7.05
105	11-1-37	10.3442	0.0003	0.018	0.1426	0.1097	0.5324	0.0056	0	0.0006	147	104	9.1	8	52.3	0.8044	1.33	0.0165	5	0	7.05
124	81-2-43	13.1909	0.0006	0.0114	0.1729	0.0855	0.1983	0.0072	0	0.0009	142	96.8	7.7	4.3	53.9	1.0226	1.17	0.0085	2.6667	0.2887	8.3
129	83-1-46	12.5705	0	0.0135	0.1701	0.0942	0.5559	0.0073	0	0.0008	156.3	93	6.4	6.3	53.8	1.3342	4.17	0.4423	4.3333	1.5275	7.55
140	147-2-50	11.5166	0.0003	0.029	0.1447	0.1215	0.1584	0.0061	0	0.0008	133.3	75	7.8	5	50.3	1.8862	3.67	0.3374	6.5	0.5	9.55
173	147-1-65	11.2916	0	0.0117	0.1488	0.1011	0.1992	0.0066	0	0.0006	165.3	77.66	16.9	10.1	53.4	1.113	1.17	0.0085	4.5	0.5	7.3
327	81-1-131	13.1865	0.0004	0.0155	0.1785	0.1022	0.1826	0.0119	0	0.0037	159.7	112.6	7.6	7.1	54.9	1.4706	1.5	0.025	6	1	8.15
	Fe Mg Sr																				
3	44-3-2	9.6425	0.0033	0.0002	0.6864	0.0915	0.0387	0.0053	0.0003	0.001					52.7	0.7033	3	0.19	1	0	7.55
116	44-2-40	10.3268	0.0253	0.0026	0.4778	0.1057	0.0038	0.0055	0	0.0008	141.2	103.2	6.2	4.6	51	1.1303	2	0.05	4.3333	1.1547	7.8
137	116-1-49	12.8435	0.0268	0.0015	0.6364	0.102	0.0046	0.0074	0	0.0011	123.1	71	5.3	3.1	52.6	3.6193	1.17	0.0085	4	1.7321	8.3
	Fe Mg No Mod.																				
7	68-3-3	9.8202	0.0015	0	0.5135	0.0768	0.0022	0.0053	0	0.0025	121			3.8	49.8	0.9688	2	0.05	1	0	7.3
	Fe Mg Na																				
11	8-3-4	9.8072	0	0.008	0.5982	0.0377	0.0056	0.0053	0.0006	0.0009	160.9	68	9.5	8.3	48.3	0.7501	1	0	4.8333	0.2887	7.3
41	8-1-14	9.6143	0	0.0028	0.6333	0.0605	0.0047	0.0056	0.0003	0.0005	119.1	92	3.5	3.5	48.9	0.9968	1.33	0.0165	1.5	0	7.3
53	44-1-18	9.5471	0.0011	0.0022	0.5474	0.0546	0.0026	0.0057	0.0003	0.0005	115.3	112	3.2	3.7	50	0.8781	1.17	0.0085	1.1667	0.2887	6.3
65	80-1-22	12.1541	0	0.0037	0.7091	0.0626	0.0036	0.0082	0.0001	0.0007					51.7	3.2872	1.17	0.0085	2	0.5	7.9
103	8-1-36	10.2812	0.0003	0.0214	0.5678	0.1086	0.0038	0.0054	0	0.0008	157.3	125.7	6.3	5	50.4	1.3586	5	0.6	5	1	7.3
126	80-2-44	12.4627	0.0005	0.0139	0.5635	0.0866	0.0054	0.0069	0	0.001	169	103.3	6.5	5	56.1	2.3312	1.67	0.0335	4.3333	1.1547	8.3
	Mg Ti Sr																				
191	55-1-73	10.1455	0.0279	0.0009	0.1394	0.0895	0.0047	0.1038	0	0.0008	147.9	98.92	6.5	5.9	49.4	1.8511	1.67	0.0335	4.5	0.5	8.8
243	127-1-90	13.2383	0.028	0.0008	0.1815	0.0979	0.0092	0.1078	0	0.0037	122.1	81.07	2.5	2.3	55.8	3.0395	1.83	0.0415	4	0	8.9
247	139-1-92	13.3996	0.0274	0.0007	0.1791	0.1021	0.0088	0.206	0	0.0039	132.6	98.1	2	2	52.2	1.7119	1.67	0.0335	3	0	11.65
	Mg Ti Na																				
159	19-1-59	10.2122	0	0.0165	0.1358	0.1	0.0054	0.1004	0	0.0006	153.8	71.7	7.2	8	51.6	0.7501	3.5	0.3	5.1667	0.2887	8.05
177	31-1-67	10.1838	0	0.0213	0.1346	0.1037	0.0038	0.1742	0	0.0006	156.5	87.5	8.7	9.2	53.4	0.6686	4.33	0.4727	4.5	0.866	12.15

	SAMPLE	Silicon	Strontium	Sodium	Iron	Magnesium	Manganese	Titanium	Boron	Copper	U.T.S.	P.S.	*A	*L	Hv10	Std. Dev.	Poro	Poro	Mod.#	Std. Dev.	Grain#
	#	%	%	%	%	%	%	%	%	%	MPa	MPa	%	%	kg/mm^2	kg/mm^2	Std. No.	Area %	AFS	AFS	ASTM
213	91-1-80	13.4535	0	0.0061	0.177	0.0965	0.0066	0.0367	0	0.0031	135.3	91.58	2.9	3	55.6	3.6501	1.17	0.0085	3.8333	0.2887	10.2
225	103-1-84	12.7762	0.0006	0.0205	0.1646	0.1051	0.0036	0.2071	0	0.0031	169.7	91.1	7.7	5.2	53.8	0.5727	3.33	0.0165	5.6667	2.2546	12.15
280	31-2-107	10.6649	0	0.0172	0.1459	0.1119	0.0042	0.1933	0	0.0029	159.2	117.4	7.1	6.4	54.4	0.9813	1.17	0.0085	4.3333	0.5774	10.9
285	91-1-110	13.3845	0.0002	0.0101	0.1734	0.1007	0.0058	0.1056	0	0.0038	139.6	76.06	3.8	4	53.5	1.608	2.5	0.12	3.6667	0.2887	8.9
309	103-1-122	12.4037	0	0.0133	0.171	0.1009	0.0056	0.2061	0	0.0032	154.3	97.94	4.2	4.6	55.3	1.3401	1.83	0.0415	5.5	2.0207	11.9
	Mg B Sr																				
	Mg B Na																				
	Mn Fe Sr																				
68	112-2-23	12.5801	0.0036	0.0024	0.6536	0.0031	0.1983	0.008	0.0003	0.0008	118.9	117.5	3.2	3.8	54.3	2.1683	1	0	1.6667	0.5774	8.8
69	114-3-23	12.8016	0.0045	0.0026	0.6686	0.0031	0.4442	0.0082	0.0003	0.0009	125	117.5	3.2	2.5	54.2	1.4665	1.33	0.0165	1.6667	1.1547	9.4
92	40-2-32	10.0226	0.0212	0.002	0.6389	0.0037	0.1983	0.0053	0	0.0008	147.6	120.4	7.8	5	47.9	2.1609	1.33	0.0165	4.8333	2.0207	7.3
114	42-4-39	10.3507	0.0225	0.0029	0.7416	0.0021	0.5397	0.0055	0	0.0009	134.2	106.3	8.2	5.3	48.1	1.401	3.33	0.2626	5	1	7.3
132	112-2-47	12.6327	0.0271	0.0022	0.6095	0.0022	0.1953	0.0074	0	0.0011	149.7	93.2	4.4	3.7	53.3	1.786	1	0	4.8333	1.6073	8.4
133	114-3-47	12.8235	0.0268	0.002	0.6237	0.0018	0.5028	0.0076	0	0.0011	126.5	95.2	3.5	3.7	50	0.6834	2.83	0.1662	3.5	1.3229	7.8
143	158-1-52	11.1878	0.0284	0.0026	0.6258	0.003	0.1904	0.007	0	0.0009	149.1	100.7	5.1	5.1	51.1	1.2561	1.17	0.0085	4.6667	2.3094	7.8
	Mn Fe No Mod.																				
36	4-2-12	9.4671	0	0.0013	0.6493	0.0006	0.2162	0.0055	0.0004	0.0006					48.6	0.8142	1.17	0.0085	1.3333	0.2887	6.3
37	6-3-12	9.6771	0	0.0017	0.6824	0.0004	0.5267	0.0055	0.0005	0.0007	118.7	75	3.5	4.3	53.9	1.5565	1.33	0.0165	1.3333	0.2887	6.3
48	40-2-16	9.5422	0	0.0008	0.608	0.0033	0.2159	0.0056	0.0004	0.0006	111.9	87	5.1	4.5	50.7	1.0013	1	0	1	0	5.8
49	42-3-16	9.6747	0	0.0007	0.6077	0.0026	0.4625	0.0056	0.0006	0.0005	120.4	90	3.5	3.7	53.7	1.5908	1	0	1.5	0	7.3
	Mn Fe Na																				
97	6-3-33	10.2404	0.0004	0.0148	0.635	0.0011	0.4718	0.0051	0	0.0009	148.9	112	11.5	8.4	50.2	0.9482	2	0.05	5	1	6.55
60	76-2-20	12.5586	0	0.0022	0.6821	0.0026	0.1915	0.0081	0.0003	0.0008	118.6		4	2.4	53.1	1.8082	1.17	0.0085	1.3333	0.2887	9.3
61	78-3-20	12.7916	0	0.0022	0.698	0.0022	0.4304	0.0082	0.0003	0.0009	126.8	109.7	4.9	4.3	55.7	1.7706	1	0	1.5	0	8.8
81	4-1-28	10.0098	0	0.0149	0.6109	0.0023	0.1948	0.0055	0.0001	0.0008	160	66.5	8.7	6.5	50.1	0.6356	3	0.19	4.3333	1.1547	7.3
120	76-2-42	12.9896	0.001	0.0185	0.5834	0.002	0.2205	0.007	0	0.0011	168.9	102.4	10.4	7.7	56.1	1.0764	4.83	0.5677	6	1	7.55
121	78-3-42	13.1782	0.0011	0.0184	0.5837	0.0021	0.5142	0.0071	0	0.0012	151.6	111.8	6.6	5.3	52.6	1.3747	1.17	0.0085	5.6667	1.5275	7.7
167	146-1-62	11.1809	0	0.0073	0.6162	0.0015	0.1977	0.0065	0	0.0008	175.7	86.3	9.2	7.2	54.7	1.6738	1	0	4	1	7.8
324	146-2-129	11.5649	0.0001	0.0113	0.608	0	0.2036	0.0106	0	0.0032	184.7	88.35	17.3	8.8	55	2.3028	1	0	4.6667	2.5166	7.8
	Mn Ti Sr																				
107	123-1-38	12.9258	0.0291	0.0024	0.1706	0.0018	0.2124	0.0931	0	0.0009	138.3	93.4	9.2	7	50.6	3.196	1.33	0.0165	3.6667	0.5774	7.95
108	135-2-38	13.1109	0.0222	0.0027	0.1717	0.0013	0.2107	0.1804	0	0.0009	126.1	73.3	5.8	3.2	50.1	1.7088	2.5	0.12	4.1667	1.0408	10.4
149	165-1-55	11.7482	0.0241	0.0009	0.1646	0.0021	0.2039	0.2307	0.0002	0.0008	147.4	123.1	7.7	9.1	49.5	1.6407	2.83	0.1662	4.3333	1.2583	12.4
171	161-1-64	11.237	0.0283	0.0002	0.1511	0.002	0.1963	0.1101	0	0.0007	150.8	65.19	11.7	10.2	47.5	0.6535	1.17	0.0085	4.6667	0.5774	8.05
188	51-2-72	9.8437	0.0281	0.0009	0.1391	0.0016	0.2095	0.0999	0	0.0006	155.4	63.9	12.6	9.8	46.6	0.5164	1.33	0.0165	4	1.3229	8.3
189	53-3-72	9.7572	0.0286	0.0009	0.1413	0.0012	0.5022	0.0982	0	0.0006	152.5	86.91	19.1	12	47.2	0.4412	1.33	0.0165	3.6667	1.4434	8.8
200	63-2-76	10.227	0.0318	0.0012	0.1473	0.0013	0.213	0.189	0	0.0025	151.4	68.88	10.1	9.8	47	0.8208	1.17	0.0085	4.3333	1.1547	12.15
201	65-3-76	10.6773	0.0336	0.0012	0.1608	0.0018	0.5106	0.2014	0.0002	0.0024	148.2	103.1	9.2	8.6	49.2	0.6178	1	0	4.5	0.866	10.05
234	123-2-87	13.1423	0.029	0.0007	0.1805	0.0023	0.1786	0.1049	0	0.0035	166	82.14	8.9	7.2	52.2	1.2336	1	0	4.6667	1.0408	8.9
235	125-3-87	13.0026	0.0217	0.0005	0.1841	0.002	0.4627	0.1018	0	0.0036	180.1	126.3	14.2	10.4	52.9	1.6327	1	0	4.1667	1.0408	8.4
246	137-2-91	13.2604	0.0273	0.0003	0.1841	0.0009	0.4981	0.1993	0	0.0038	136.4	84.31	4.6	4.7	53.6	1.275	1	0	4.5	0.5	11.15

	SAMPLE	Silicon	Strontium	Sodium	Iron	Magnesium	Manganese	Titanium	Boron	Copper	U.T.S.	P.S.	*A	*L	Hv10	Std. Dev.	Poro	Poro	Mod.#	Std. Dev.	Grain#
	#	%	%	%	%	%	%	%	%	%	MPa	MPa	%	%	kg/mm^2	kg/mm^2	Std. No.	Area %	AFS	AFS	ASTM
	Mn Ti Na																				
147	149-1-54	11.5265	0	0.0104	0.1667	0.0021	0.2028	0.1053	0.0002	0.0009	171.1	80.3	16.3	12.2	52.5	1.5069	1.17	0.0085	4.3333	0.5774	8.05
156	15-2-58	10.3232	0	0.02	0.1515	0.0032	0.2231	0.0977	0.0002	0.0008	141.1	64.3	7.7	8.7	49.6	0.3869	1	0	5.3333	0.5774	8.3
157	17-3-58	10.1016	0.0002	0.0156	0.144	0.0018	0.5021	0.0887	0	0.0007	160	68.5	11.2	12.5	51.1	0.5231	1	0	4.6667	1.0408	7.3
169	153-1-63	11.2818	0	0.0082	0.1496	0.0017	0.1897	0.1996	0	0.0007	169.2	75.27	9.7	9	49.2	0.9668	1	0	4.3333	0.5774	12.4
170	154-2-63	11.542	0	0.0105	0.2236	0.001	0.1872	0.1994	0	0.0008	164.7	103.2	8.5	7.7	50.5	1.186	1	0	4.6667	0.5774	11.9
184	27-2-70	9.7786	0	0.014	0.1314	0.0007	0.1703	0.2329	0	0.0006	168.2	94.58	19.4	14.6	48.6	0.3869	1	0	5.1667	0.2887	13.65
185	29-3-70	9.9225	0	0.0105	0.1383	0.0002	0.4804	0.2351	0	0.0006	169	78.5	12.8	11.9	51.7	1.4878	1	0	4.6667	0.5774	12.9
210	87-2-79	13.1788	0	0.0131	0.1786	0.0007	0.2257	0.1016	0	0.0038	176	94.11	11.8	9.2	53.4	1.0075	1.33	0.0165	5.8333	1.0408	8.2
211	89-3-79	13.1643	0	0.0132	0.1827	0.0001	0.5232	0.0983	0	0.0037	172.2	83.73	8.9	6.8	54	4.0112	1	0	5.6667	1.2583	7.7
222	99-2-83	12.9626	0.0006	0.0142	0.1729	0.0018	0.2127	0.1875	0	0.0036	160.6	118.6	7	6.1	55.8	1.7725	1	0	6	1.7321	11.15
223	101-3-83	13.1802	0.0004	0.0186	0.179	0.0013	0.551	0.1858	0	0.004	140.8	104.8	3.9	2.4	55.9	2.147	1.17	0.0085	7.1667	0.2887	10.4
332	153-2-133	11.7629	0	0.0127	0.1677	0.0006	0.214	0.2207	0	0.0032	165.5	90.81	9.7	12	51.5	0.455	4	0.41	6.3333	1.1547	11.9
	Mn B Sr																				
412	254-1-195.	11.519	0.0148	0.0001	0.292	0.0016	0.2005	0.0036	0.042	0.0011	117.2	100.8	1.3	1.6	50.7	0.8672	4.17	0.4423	1.3333	0.5774	13.4
486	294-1-269.	12.2966	0.0153	0	0.3052	0.0019	0.0045	0.0224	0.0013	0.001	138.5	90.42	8	5.4	51.8	0.3937	1	0	3.5	0.5	9.3
	Mn B Na																				
	Fe Ti Sr																				
193	50-1-74	9.847	0.0312	0.0006	0.5824	0.0022	0.0039	0.0805	0	0.0007	151.6	74.5	8.5	7.3	47	0.2898	1.5	0.025	4.8333	0.2887	9.05
205	62-1-78	10.3282	0.0282	0.0013	0.5993	0.0015	0.004	0.1732	0	0.0028	156.9	98.83	8.3	6.5	48.8	1.2449	1.33	0.0165	4.5	0.866	12.05
239	122-1-89	13.0341	0.0214	0.0006	0.6757	0.0025	0.0081	0.1054	0	0.0038	136.8	86.43	2.5	2.2	54.7	1.2044	1.17	0.0085	4.1667	0.7638	8.4
281	50-1-108	10.5588	0.0255	0.0009	0.5644	0.0029	0.0065	0.1039	0	0.0029	162.9	88.49	11.6	9	49	0.9395	1	0	5	0.5	8.3
360	134-1-151.	12.501	0.0326	0.0001	0.6644	0.0025	0.0125	0.2038	0	0.0019	145.1	132	2.3	2.7	55.4	2.8548	1	0	4.1667	0.5774	10.05
	Fe Ti Na																				
161	26-1-60	9.9126	0	0.0112	0.581	0.0009	0.0038	0.1886	0	0.0007	163.7	68.9	8.2	8.2	50.6	1.1537	1.33	0.0165	5.8333	1.0408	12.4
181	14-1-69	10.1519	0	0.014	0.4431	0.0024	0.0053	0.1042	0	0.0008	166	88.98	12.6	11.4	50.7	1.1793	2.5	0.12	4.6667	0.5774	8.05
215	86-1-81	12.9709	0.0002	0.0176	0.6031	0.0021	0.0073	0.1038	0	0.0041	182.8	93.3	7	6.7	53.6	2.3022	4.83	0.5677	6.1667	1.0408	9.3
227	98-1-85	12.8823	0.0003	0.0189	0.5925	0.0017	0.008	0.1982	0	0.0037	148.9	93.02	7.5	6.7	54.8	1.4962	4.5	0.505	6.6667	0.5774	11.65
271	14-1-103	10.6048	0	0.0122	0.6	0.002	0.0058	0.1046	0	0.0032	178.7	133.2	10.9	9.8	52.5	0.7679	1	0	5	0	8.3
	Fe B Sr																				
390	269-1-173.	11.618	0.0137	0.0001	0.2955	0.0016	0.0046	0.001	0.037	0.003	110.5	81.97	0.5	2.9	47.7	1.04	3.67	0.3374	1.3333	0.2887	12.8
417	260-1-200.	11.636	0.0159	0.0001	0.3423	0.0021	0.0112	0.0033	0.0469	0.0011	115.7	89.54	2	1.6	50.3	1.8801	1.17	0.0085	1.5	0	13.4
437	240-1-220.	11.9236	0.0384	0	0.2994	0.0025	0.0102	0.0096	0.0334	0.001	114.5	87.95	3	2	50.2	1.1003	3.17	0.2274	1.6667	0.2887	10.8
	Fe B Na																				
	Ti B Sr																				
345	238-1-140.	12.1312	0.0314	0.0003	0.2909	0.0014	0.0035	0.0976	0.0103	0.0012	126.5	87.7	3.1	3.2	49.3	1.3197	4	0.41	2.6667	1.0408	7.95
346	240-2-140.	12.0457	0.0637	0.0003	0.2934	0.0015	0.0013	0.0887	0.0075	0.0013	128.9	89.6	2.9	4.4	48.9	3.6746	3.5	0.3	3.5	0.866	9.3
349	274-1-142.	12.4261	0.0304	0.0002	0.2903	0.0015	0.0086	0.1979	0.0023	0.0014	146.9	104	5.1	6.3	52.2	1.1754	2	0.05	3.5	1.3229	11.4
351	275-1-143.	12.3895	0.0269	0.0002	0.2894	0.0018	0.0076	0.1634	0.0056	0.0014	125.8	116	4	4.5	49.7	0.9621	1.67	0.0335	3	0	11.9
353	276-1-144.	12.5291	0.0248	0.0001	0.2598	0.0029	0.0067	0.1501	0.0072	0.0016	124.1	110	2.5	3.6	50.3	1.6909	1.67	0.0335	3.8333	1.2583	10.4
355	236-1-146.	12.2222	0.0088	0.0001	0.2942	0.0014	0.0037	0.0849	0.006	0.0012	135.2	83.6	4.7	4.1	49.5	0.6812	1.33	0.0165	3.6667	1.2583	9.05
361	215-1-152.	11.7996	0.0246	0	0.2811	0.0012	0.0034	0.0945	0.0081	0.003	130.8	118	3.6	5.2	48.7	1.9045	2.17	0.0738	3.1667	1.7559	9.3
362	221-2-152.	11.8424	0.0467	0.0001	0.2805	0.0014	0.0043	0.0964	0.0089	0.0024	136.2	119	5.8	5.1	48.9	1.3461	1	0	3.5	0.5	8.3

	SAMPLE	Silicon	Strontium	Sodium	Iron	Magnesium	Manganese	Titanium	Boron	Copper	U.T.S.	P.S.	*A	*L	Hv10	Std. Dev.	Poro	Poro	Mod.#	Std. Dev.	Grain#
	#	%	%	%	%	%	%	%	%	%	MPa	MPa	%	%	kg/mm^2	kg/mm^2	Std. No.	Area %	AFS	AFS	ASTM
367	240-1-154.	12.2787	0.0423	0.0001	0.2735	0.0013	0.0034	0.0832	0.0041	0.0012	131.4	113	3.2	4.6	47.6	0.343	2.5	0.12	3.1667	0.7638	7.8
368	209-1-155.	10.1945	0.0249	0	0.228	0.001	0.0032	0.1073	0.0131	0.0032	130	118	5.3	4.6	45.5	1.8349	3.83	0.3726	3.6667	0.2887	10.55
369	274-1-155.	12.4842	0.0273	0	0.2822	0.0014	0.0079	0.2015	0.0058	0.0014	123.6	114	3.7	2.9	47.7	1.897	3	0.19	3.5	2.2913	12.9
371	275-1-156.	12.0827	0.0268	0	0.2664	0.0022	0.008	0.1282	0.0049	0.0013	124	112	2.9	3.1	48.2	1.2513	1.5	0.025	3.3333	1.5275	8.9
372	221-1-156.	12.6717	0.0261	0.0003	0.2674	0.0029	0.0081	0.1167	0.0144	0.0036	116.8	110	0.2	2.6	48.5	0.8311	3.17	0.2274	2.6667	2.0207	8.3
377	275-1-160.	12.2362	0.0156	0.0005	0.2595	0.0033	0.013	0.1342	0.0046	0.002	131.1	64.1	2.5	4.3	50	0.9099	5.67	0.9149	2.5	1.5	10.4
388	277-1-171.	11.9883	0.016	0.0002	0.2909	0.0017	0.0048	0.0435	0.0038	0.0033	127.6	80.59	3.2	5	47	0.7589	4.33	0.4727	3	0.5	9.3
391	282-1-174.	12.1949	0.0188	0.0002	0.2904	0.0016	0.0049	0.0792	0.0045	0.0029	130	83.9	3.1	3.8	48.6	0.9109	1.33	0.0165	4.6667	0.2887	8.55
398	214-1-181.	11.715	0.0182	0.0001	0.2626	0.002	0.0035	0.0339	0.0024	0.0014	124.8	91.9	3.4	4.6	48.1	1.0602	1.5	0.025	4.3333	0.7638	9.3
409	235-1-192.	11.5129	0.0103	0.0001	0.2887	0.0016	0.0036	0.0101	0.0637	0.0479	121.6	93.78	1.8	2.3	47	1.2797	1	0	1	0	13.15
415	267-1-198.	11.9166	0.0245	0.0001	0.2884	0.0018	0.0072	0.0108	0.0366	0.0012	120.9	86.88	1.2	1.7	49.2	0.9709	6	1.07	1.3333	0.2887	13.4
420	216-1-203.	11.7326	0.0227	0.0002	0.2847	0.0014	0.0036	0.207	0.064	0.0033	129.9	104.1	3.1	4.9	49.3	0.625	1.17	0.0085	3.6667	0.7638	8.2
425	210-1-208.	9.7673	0.0328	0.0001	0.2377	0.0013	0.0035	0.4228	0.1289	0.0008	131.8	58.8	7.6	6.9	45.6	0.502	1.17	0.0085	4.8333	0.7638	9.3
427	239-1-210.	11.4058	0.0692	0.0003	0.287	0.0016	0.0043	0.0145	0.0809	0.0012	118.4	105	2.2	2.4	48.3	0.8841	3.5	0.3	1.5	0.5	12.4
432	275-1-215.	12.0781	0.0355	0.0001	0.2873	0.0018	0.0043	0.3175	0.0698	0.0012	133.6	70.86	3.4	3.8	50	1.3352	1	0	4	0.5	8.3
435	210-1-218.	9.9532	0.0278	0.0001	0.2207	0.0017	0.0032	0.1854	0.0655	0.0007	133.2	70.2	6.9	6.5	46.5	1.7213	3	0.19	3.8333	0.5774	9.8
441	222-1-224.	12.8798	0.0374	0.0002	0.2933	0.0027	0.0088	0.2261	0.0672	0.0022	164.7	90.88	9.1	7.2	50.5	0.8	2	0.05	4.6667	0.5774	8.05
447	237-1-230.	12.1791	0.0171	0.0007	0.2909	0.0023	0.0048	0.2821	0.0876	0.0012	137.9	102.3	5.4	5	50.6	1.0801	2	0.05	4	1.7321	10.55
450	251-1-233.	11.7556	0.0493	0.0002	0.284	0.004	0.0047	0.0252	0.0668	0.0012	115.6	88.02	0.2	2.3	50.1	1.9854	5	0.6	1.3333	0.2887	12.4
459	277-1-242.	12.2916	0.0543	0.0002	0.2906	0.0019	0.0048	0.1753	0.0552	0.0012	136.8	88.29	4.7	5.3	47.8	1.3556	2.5	0.12	4.5	0	9.8
460	275-1-243.	12.2873	0.0374	0.0001	0.2778	0.0019	0.0047	0.3427	0.0753	0.0012	136.7	113.1	4.1	4.5	49.7	1.054	1.17	0.0085	5	0	8.3
461	276-1-244.	12.5235	0.0415	0	0.292	0.0017	0.0045	0.2755	0.0785	0.0012	136.5	69	6.7	5.9	48.5	1.742	3	0.19	4.3333	0.7638	9.3
	Ti B No Mod.																				
337	224-1-136.	12.0391	0	0.0002	0.168	0.0022	0.0032	0.0999	0.011	0.0017	116	95.03	1.4	4.4	50	1.8016	1.83	0.0415	1.5	0.5	10.65
401	225-1-184.	11.4939	0.0002	0.0003	0.2579	0.0023	0.0044	0.0435	0.0026	0.0016	110.3	66.82	0	2.2	50.9	1.008	2	0.05	1	0	9.8
442	225-1-225.	12.0653	0.001	0.0005	0.2906	0.0021	0.0048	0.2029	0.0622	0.0012	108.9	97.06	5.5	2.9	51.5	1.9776	5.83	0.9901	1	0	8.8
	Ti B Na																				
336	212-2-135.	11.3365	0	0.0118	0.1641	0.0004	0.0054	0.1368	0.0191	0.0029	148.5	103.6	6.7	8.9	50.1	0.7005	5	0.6	4.6667	2.0817	10.9
338	227-2-136.	12.3005	0.0001	0.0057	0.1727	0.0018	0.004	0.0891	0.0079	0.0019	162.7	93.54	10.9	10	52.2	2.5787	5.17	0.6799	3	1	8.15
343	218-1-139.	12.4352	0.0007	0.0131	0.2917	0.0017	0.0103	0.0936	0.0094	0.0018	164	108	12.3	8.8	52.8	2.1433	1.83	0.0415	5.6667	1.6073	11.15
344	233-2-139.	12.3213	0	0.0212	0.2902	0.0006	0.0103	0.0866	0.0071	0.0019	144.9	106	10.3	7.3	52.4	2.198	1.83	0.0415	7.1667	1.0408	11.4
363	230-1-153.	12.3162	0	0.0098	0.2871	0.0014	0.0034	0.096	0.0085	0.0014	167.6	117	8.4	9.3	52.8	1.4566	2	0.05	5.6667	0.5774	8.9
364	233-2-153.	12.3873	0	0.0245	0.2818	0	0.0042	0.0815	0.0046	0.0016	154.1	115	10.1	8.6	51.6	1.9202	1.33	0.0165	7.6667	0.5774	11.4
365	206-1-154.	10.0913	0	0.0072	0.2075	0.0012	0.0038	0.1153	0.0168	0.0048	164.6	128	13.2	10.1	49.1	1.0747	6	1.07	4.1667	2.0207	8.2
374	233-1-157.	12.3788	0	0.0249	0.2596	0.0011	0.0125	0.1062	0.0123	0.0021	159.9	99.2	12.2	10.1	51	1.4922	1.83	0.0415	8	0	12.15
386	233-1-169.	12.3129	0	0.0167	0.2301	0.0011	0.0031	0.1521	0.0259	0.0143	152	75.3	10.5	9.2	52.1	2.1204	3	0.19	7.3333	0.5774	10.9
395	207-1-178.	9.876	0	0.009	0.2353	0.0013	0.0031	0.0734	0.0063	0.0152	157.6	70.5	12.3	11.4	46.6	0.6676	1	0	5.6667	0.5774	9.3
397	211-1-180.	11.5727	0	0.0095	0.2868	0.0012	0.0035	0.0457	0.0051	0.0023	168.9	77.96	9.1	8.6	49.8	0.7985	1.17	0.0085	5.5	0.5	10.05
402	207-1-185.	9.9704	0	0.0178	0.2215	0.0009	0.0035	0.351	0.1188	0.0013	148.9	70.5	11.5	10.5	47.7	1.5306	1.5	0.025	6	0.866	10.3
403	211-1-186.	11.4355	0	0.009	0.2782	0.0007	0.0036	0.0146	0.0715	0.0011	168.3	92.3	9.7	9.9	49.5	2.847	1.17	0.0085	4.6667	0.2887	13.4
418	233-1-201.	12.112	0.0001	0.0329	0.229	0.0012	0.0043	0.1549	0.0303	0.001	163.6	87.15	3.1	9.3	52.8	2.0253	6	1.07	7.1667	0.7638	10.4
419	213-1-202.	11.8079	0	0.0149	0.2824	0.0015	0.0039	0.3498	0.104	0.0026	153.8	101.9	3.7	6.3	53.5	0.8556	1.17	0.0085	7.5	0.866	9.4
424	207-1-207.	9.6469	0	0.014	0.2378	0.0013	0.0041	0.4066	0.1254	0.001	155	62.4	10.8	8.5	48.4	0.8472	6	1.07	6.5	0.5	10.55
426	233-1-209.	12.0957	0	0.0279	0.2894	0.0007	0.0043	0.076	0.0075	0.0012	151.9	115.2	2	6.7	53.1	1.6425	1	0	7	1.7321	11.15
434	207-1-217.	9.9689	0	0.0185	0.2421	0.001	0.0031	0.1652	0.0565	0.0009	152.6	63.15	9	9.3	47.6	0.5046	1.17	0.0085	6.3333	1.5275	10.3
439	213-1-222.	12.2416	0	0.0143	0.2896	0.0015	0.0103	0.2319	0.0731	0.0014	163.8	83.5	11	9.3	52.2	1.3054	5.67	0.9149	6.5	0.866	10.9
440	219-1-223.	12.7027	0.0011	0.014	0.2949	0.0023	0.0091	0.2082	0.0645	0.0019	140.7	116.6	5.1	5.7	53.4	1.9232	1.17	0.0085	7	1	11.9
443	228-1-226.	12.3312	0.0001	0.0058	0.2944	0.0018	0.0051	0.1769	0.0533	0.0012	148.6	105.6	2.7	5.4	52.6	1.1041	3	0.19	4	0.5	8.3

	SAMPLE	Silicon	Strontium	Sodium	Iron	Magnesium	Manganese	Titanium	Boron	Copper	U.T.S.	P.S.	*A	*L	Hv10	Std. Dev.	Poro	Poro	Mod.#	Std. Dev.	Grain#
	#	%	%	%	%	%	%	%	%	%	MPa	MPa	%	%	kg/mm^2	kg/mm^2	Std. No.	Area %	AFS	AFS	ASTM
444	233-1-227.	12.2915	0	0.0246	0.2868	0.0007	0.0045	0.0807	0.0102	0.0014	158.3	100.7	10.1	9.3	52.7	2.0147	5.33	0.7551	7	1.7321	11.15
446	231-1-229.	12.5104	0	0.0155	0.2881	0.0014	0.0048	0.2042	0.0642	0.0014	166.6	88.22	9.2	9.5	53.4	1.679	4.5	0.505	6.1667	1.6073	10.9
472	234-1-255.	12.1367	0	0.0215	0.2765	0.0017	0.0117	0.4412	0.1354	0.0012	159.1	117.9	6.4	10.2	49.6	1.4348	5.5	0.835	7	1	10.9
479	234-1-262.	12.2023	0	0.032	0.284	0.001	0.0043	0.0651	0.018	0.0011	161.9	93.69	5.5	9.8	52.8	2.147	1	0	7.6667	0.5774	11.65
	Mn Fe Mg Sr																				
14	120-2-5	12.636	0.0199	0.0001	0.7126	0.1173	0.4424	0.0073	0.0004	0.0009	136.5	100	4.5	2.4	54.7	1.6601	4.33	0.4727	2.6667	0.5774	7.8
16	108-2-6	12.6402	0.0145	0.0001	0.8376	0.1289	0.4786	0.0075	0.0005	0.0022	134.6	115.5	1.4	3.7	56.6	2.9228	5.33	0.7551	3	1	7.3
73	118-1-25	9.7574	0.0262	0.0001	0.5806	0.1045	0.2105	0.008	0.0001	0.0007	136.7	112.5	4	2.8	52.6	3.0874	3	0.19	3.8333	0.2887	7.2
74	120-2-25	9.6658	0.0293	0.0002	0.5821	0.0761	0.529	0.0081	0.0001	0.0009	118.4	107.5	4.9	3.9	52.1	1.1553	2.17	0.0738	3.3333	0.7638	7.3
80	195-2-27	11.5151	0.0256	0.0029	0.6738	0.0995	0.4716	0.0065	0.0001	0.001	127.4	72.55	3.2	3.5	52	1.7268	2.83	0.1662	3.6667	1.1547	7.8
93	46-3-32	10.2572	0.021	0.0038	0.4274	0.0859	0.1951	0.0053	0	0.0009	155	108	7.7	4.3	54.2	0.9309	1.33	0.0165	3	0	6.8
94	48-4-32	10.1588	0.0197	0.0036	0.6277	0.077	0.4351	0.0052	0	0.0009	149.9	104.2	8.2	6.8	52.7	1.4255	1.5	0.025	3.6667	0.5774	7.3
134	120-4-47	12.9183	0.031	0.0022	0.6039	0.1161	0.4865	0.0075	0	0.0012					55	1.4529	2.17	0.0738	4.5	0.5	8.55
138	118-2-49	12.9175	0.0234	0.0016	0.6482	0.1173	0.1761	0.0075	0	0.0011	138.6	80	2.3	3.5	56.1	3.0083	1.67	0.0335	4	1	8.05
144	160-2-52	11.2731	0.0255	0.0022	0.6111	0.1162	0.1862	0.007	0	0.0009	135	90.87	4.1	2.9	53	3.0466	2.83	0.1662	4.1667	2.3629	7.3
329	120-1-132	12.9434	0.0255	0.0005	0.7652	0.1031	0.5973	0.0111	0	0.004	129.9	106.4	3.7	2.5	58.8	1.6351	1.17	0.0085	3.5	0.5	7.7
	Mn Fe Mg No Mod.																				
4	48-4-2	9.8345	0.0011	0	0.7019	0.085	0.4644	0.0051	0.0004	0.0009	130	61	3	4.4	53.9	1.0496	4.67	0.5373	0.5	0	7.8
8	72-4-3	9.5169	0	0	0.5488	0.069	0.4387	0.0051	0.0004	0.0027	123.3	62.46	4.6	3.6	51.1	2.1085	5.83	0.9901	1.5	0	6.8
42	10-2-14	9.8201	0	0.0017	0.6654	0.033	0.177	0.0058	0.0003	0.0007	113.6	98	3.5	5.2	50.5	0.7633	1	0	1.1667	0.2887	6.3
50	48-4-16	10.0679	0.0009	0.0009	0.6164	0.0371	0.4647	0.0059	0.0004	0.0008	122.2	88.72	4	3.5	53.5	2.4574	1	0	1.5	0	7.55
70	120-4-23	13.0356	0.0027	0.0026	0.6577	0.0473	0.4318	0.0085	0.0003	0.0011	113.5	90.3	2	1.8	56.3	3.633	1.5	0.025	2	0	9.65
	Mn Fe Mg Na																				
12	12-4-4	9.531	0	0.0037	0.6059	0.0265	0.578	0.0051	0.0005	0.001	139.1	63.5	7.6	8.8	50.4	2.2115	1.17	0.0085	3	0.5	7.05
21	188-1-8	11.1357	0	0.0114	0.669	0.1015	0.4636	0.0062	0.0004	0.0022					53.7	1.7989	3.83	0.3726	4	0	7.8
22	189-2-8	10.8516	0	0.0242	0.6454	0.0813	0.4952	0.006	0.0004	0.0022	153.1	80.7	6.5	6.5	54.9	2.303	5.83	0.9901	6.6667	0.5774	7.8
23	190-3-8	11.1015	0	0.0351	0.6115	0.0622	0.5144	0.0058	0.0006	0.0022	148.8	74.2	5.8	7.2	54.7	1.1737	4.67	0.5373	7	0	7.3
24	191-4-8	10.9934	0	0.0483	0.6058	0.0442	0.5377	0.0056	0.0004	0.0023	139.1		10.3	9	52.9	0.8262	6	1.07	7.1667	1.0408	7.8
38	12-4-12	10.0949	0	0.0029	0.7536	0.0676	0.5228	0.0056	0.0006	0.0009	124.7	102	6.3	5.4	53.4	1.0328	1	0	1	0	8.3
54	46-2-18	9.9149	0.0006	0.0024	0.5624	0.0296	0.2003	0.0057	0.0003	0.0006					49.8	1.6869	1.17	0.0085	1.5	0.5	7.3
62	84-4-20	13.1415	0	0.0043	0.7046	0.0472	0.4176	0.0086	0.0003	0.001	128	109	7.1	5.2	55.7	1.4542	1	0	2.3333	0.5774	8.3
66	82-2-22	12.8014	0	0.0028	0.7219	0.0393	0.1753	0.0086	0.0002	0.0009	121.6	115.7	2.5	2.5	54.8	0.9432	1	0	1.5	1.3228	9.05
71	10-1-24	9.7238	0	0.0146	0.626	0.1002	0.198	0.0081	0	0.0008	144	114	4.4	5.3	54.9	2.2528	4	0.41	5	1	8.05
72	12-2-24	9.654	0	0.0093	0.6467	0.0822	0.5116	0.0084	0	0.0008	131.5	122.1	4.9	4.6	53.9	2.3441	2.33	0.0962	4	0	7.9
78	84-4-26	14.0016	0	0.0068	0.5132	0.0808	0.4742	0.0083	0	0.0018	121.8	73	5.8	2.7	57.2	1.4665	3.17	0.2274	2.3333	0.5774	8.4
82	12-2-28	9.9993	0	0.0106	0.6061	0.0791	0.4476	0.0053	0.0001	0.0009	148.1	109.6	9.9	6.1	50.9	0.7501	2.67	0.1438	3	0	6.8
86	84-2-30	13.1544	0.0009	0.0135	0.5155	0.1285	0.4471	0.007	0	0.0011	165.2	113.9	4.7	5.7	55.6	2.3712	2	0.05	3.6667	1.1547	8.3
98	12-4-33	10.393	0.0007	0.0168	0.622	0.0786	0.4629	0.0052	0	0.0009	149.8	111.2	7.7	7.3	52	1.6315	1.5	0.025	5.3333	0.5774	6.8
122	84-4-42	13.4159	0.0012	0.0204	0.5746	0.1421	0.5005	0.0072	0	0.0012	148.1	105.6	2.5	4.5	58.7	1.3977	3	0.19	4.6667	0.5774	11.4
127	82-1-45	12.7287	0	0.0118	0.6273	0.0989	0.1878	0.007	0	0.001	175.3	103	5.9	5.9	57.4	1.9209	2.83	0.1662	3.8333	1.0408	8.3
168	148-2-62	11.4096	0	0.0108	0.6166	0.1141	0.2334	0.0065	0	0.0008	172.2	90.14	5.6	5.3	55.6	1.7037	1.07	0.0035	4.5	0.866	7.3
	Mn Mg Ti Sr																				
109	143-3-38	13.1895	0.0268	0.0031	0.1736	0.1158	0.4963	0.1739	0	0.0011	130.6	98.1	3.9	2.8	57.3	0.5854	3	0.19	4	1	9.55
151	163-1-56	11.5882	0.0294	0.0016	0.163	0.116	0.2169	0.1157	0.0002	0.0008	131.1	69.2	4.3	4.6	54.7	2.1824	1.17	0.0085	4.6667	1.0408	8.05
152	167-2-56	11.6206	0.0255	0.0017	0.1626	0.1304	0.2155	0.2265	0.0002	0.0009	137.8	79	3.2	3.8	54.1	1.7882	1.17	0.0085	4.8333	0.7638	12.9
192	57-2-73	10.189	0.0299	0.0009	0.1409	0.1219	0.0669	0.103	0	0.0008	133.5	75.55	5.5	4.1	53.1	2.3192	2	0.05	4.1667	1.0408	7.8

	SAMPLE	Silicon	Strontium	Sodium	Iron	Magnesium	Manganese	Titanium	Boron	Copper	U.T.S.	P.S.	*A	*L	Hv10	Std. Dev.	Poro	Poro	Mod.#	Std. Dev.	Grain#
	#	%	%	%	%	%	%	%	%	%	MPa	MPa	%	%	kg/mm^2	kg/mm^2	Std. No.	Area %	AFS	AFS	ASTM
190	59-4-72	9.7237	0.0299	0.0006	0.1403	0.1122	0.4904	0.0959	0	0.0006	148	99.81	4.1	4.2	55.1	2.306	1.17	0.0085	4.3333	0.2887	7.55
202	71-4-76	10.6665	0.0402	0.0012	0.1561	0.1224	0.5137	0.1951	0.0005	0.0024	141.1	81.74	1.3	3.7	55.5	2.0442	5	0.6	4.5	0.866	9.3
203	67-1-77	10.5111	0.0283	0.0013	0.1491	0.1128	0.1669	0.1991	0	0.0026	125.6	82.34	3.4	4	55.9	1.4052	1	0	4.3333	1.6073	11.8
204	69-2-77	10.926	0.0318	0.0017	0.1607	0.1238	0.1725	0.2122	0.0001	0.0023	137.9	83.79	4.8	4.6	52.2	0.8841	1	0	4.1667	1.0408	12.3
236	131-4-87	13.2215	0.0227	0.0004	0.1807	0.0882	0.4483	0.102	0	0.0038	137.4	92.6	2.5	2.6	55.1	1.8291	1.17	0.0085	3.5	0.5	7.95
244	129-2-90	13.0695	0.0286	0.0005	0.1878	0.1189	0.1768	0.1039	0	0.0038	139.3	94.91	2.5	3.1	56.1	2.8904	3.67	0.3374	3.6667	0.5774	8.4
248	141-2-92	13.4224	0.0281	0.0004	0.1795	0.0892	0.2283	0.2013	0	0.004	128.3	98.32	0.4	2.6	55.3	1.8019	3.67	0.3374	3.6667	0.2887	10.9
275	57-1-105	10.434	0.0268	0.0006	0.151	0.1049	0.1999	0.0674	0	0.0027	138.5	108.2	5.8	3.2	53.4	2.1759	1.17	0.0085	4.1667	0.7638	8.8
283	57-1-109	10.7822	0.0271	0.0012	0.1521	0.1086	0.2051	0.1031	0	0.0021	122.9	89.52	3.6	3.8	55.4	2.2364	2	0.05	3.5	0.5	8.8
284	71-2-109	10.8045	0.0336	0.0009	0.1515	0.12	0.5048	0.2084	0	0.003	135.5	110.6	3.1	2.9	55.2	1.2644	1.17	0.0085	3.8333	0.7638	12.9
	Mn Mg Ti Na																				
106	35-2-37	10.5887	0.0004	0.014	0.142	0.1023	0.5217	0.1651	0	0.0007	161.6	118.9	9.4	7.5	56.2	4.084	1.33	0.0165	5	1	8.9
130	95-2-46	12.6417	0	0.0125	0.1692	0.0934	0.5431	0.0751	0	0.0009	162	115.3	7.7	5.1	53.4	1.4473	3.83	0.3726	4	0.5	8.8
141	151-1-51	11.3835	0.0001	0.0147	0.1455	0.1047	0.1436	0.0999	0	0.0008	155.1	70.6	5.8	6.3	52	1.0289	1.5	0.025	4.3333	1.1547	8.05
142	155-2-51	11.3751	0.0003	0.0214	0.143	0.1099	0.1391	0.1832	0	0.0008	148.7	88.8	6.6	6.7	53	1.0558	5.67	0.9149	4.5	1.3229	12.4
158	23-4-58	10.0583	0.0001	0.0215	0.1408	0.1319	0.4923	0.0876	0	0.0006	158.4	73.4	7.2	6.9	53	5.059	2.67	0.1438	4.8333	0.7638	6.8
160	21-2-59	10.4138	0	0.0158	0.1524	0.1329	0.2081	0.1084	0.0002	0.0008	160.9	86.4	7.3	8.1	53.3	0.7772	3.83	0.3726	4.6667	1.4434	7.55
174	155-2-65	11.4825	0	0.013	0.1488	0.1129	0.1943	0.2019	0	0.0007	167.8	83.1	7.7	5.6	56.7	1.2485	1.17	0.0085	4	1	12.9
178	33-2-67	10.0451	0	0.017	0.1347	0.114	0.1722	0.2013	0	0.0006	162.3	106.7	7.6	7.8	54.3	1.3338	4.33	0.4727	4	1	12.9
186	35-4-70	9.9084	0	0.0188	0.1348	0.1197	0.4641	0.2262	0	0.0006	163.2	78.59	6.7	9.3	56.5	1.7661	1.17	0.0085	4.5	0.5	12.15
212	95-4-79	13.5643	0	0.0137	0.1867	0.111	0.5111	0.0994	0	0.004	169.9	109.7	7.2	5.5	58.1	1.3486	1.17	0.0085	5	1.7321	8.4
214	93-2-80	13.2059	0	0.0072	0.1816	0.1006	0.2066	0.155	0	0.0034	182.7	124.6	2.8	4.1	56.6	2.352	1.5	0.025	3.3333	0.7638	10.4
224	107-4-83	13.0867	0.0001	0.0198	0.1767	0.1454	0.5313	0.177	0	0.0041	130.6	105.2	2	2.2	59.1	2.0265	4.67	0.5373	6.1667	1.5275	9.4
226	105-2-84	12.8884	0.0005	0.0151	0.1701	0.1153	0.1919	0.2055	0	0.0033	170.6	87.98	5.4	4.9	56.5	0.9913	1.5	0.025	4.3333	0.5774	11.65
286	93-2-110	13.4737	0.0002	0.0145	0.1763	0.1028	0.1075	0.103	0	0.004	158.1	88.33	5.7	5.2	53.5	1.7111	1.67	0.0335	5.5	2.5981	9.4
310	107-2-122	12.4827	0.0001	0.0136	0.1783	0.1072	0.5965	0.1967	0	0.0034	150	113.7	3.9	3.8	57.2	2.225	1.5	0.025	5.1667	1.2583	10.65
	Mg Mn B Sr																				
495	RMZ	11.5414	0.0223	0.0007	0.2911	0.0218	0.0955	0.0082	0.0104	0.0058	129.7	66	3.4	4.7	46.8	2.4768	1	0	3.5	1.3229	11.4
	Mg Mn B Na																				
	Mg Fe Ti Sr																				
165	68-1-61	10.0103	0.0244	0.0003	0.5756	0.1026	0.004	0.1853	0	0.0008	142.5	73	4.3	4.1	53.5	2.1134	3.33	0.2626	4.3333	1.1547	11.4
197	56-1-75	10.0606	0.0284	0.0008	0.5795	0.106	0.0042	0.1026	0	0.0007	158	85.42	5	5.1	53.8	0.7714	1.33	0.0165	4.5	0.5	8.55
198	58-2-75	10.1168	0.0319	0.0008	0.5801	0.1391	0.028	0.1012	0	0.0007	145.4	91.93	4.7	4.2	56.1	1.0386	1.67	0.0335	4.3333	0.7638	8.3
237	128-1-88	13.1452	0.0234	0.0007	0.6116	0.099	0.0076	0.11	0	0.0045	141.1	92	1.4	2.2	56.1	4.5146	3.83	0.3726	3.3333	0.2887	8.3
249	140-1-93	13.1925	0.0274	0.0008	0.6424	0.109	0.0077	0.2072	0	0.004	135.9	100.1	2.1	1.8	57.7	1.81	4.83	0.5677	3.5	0	11.9
	Mg Fe Ti Na																				
175	32-1-66	10.1241	0	0.0233	0.5677	0.1084	0.0048	0.169	0	0.0008	157.6	90.3	3.9	3.8	57.2	1.0633	3.17	0.2274	5	1	12.4
179	20-1-68	9.9955	0	0.0098	0.5888	0.0994	0.0036	0.1008	0.0001	0.0008	158.6	96.61	5.1	4.6	55.7	1.4123	3.17	0.2274	3.8333	1.2583	8.05
219	92-1-82	13.3944	0	0.0209	0.6688	0.0976	0.0066	0.1032	0	0.0036	167.6	91.31	2.5	3.8	60.3	1.2828	1.17	0.0085	4.6667	2.0817	9.15
231	104-1-86	13.1583	0.0002	0.0096	0.5961	0.0997	0.0075	0.1966	0	0.0038	183.1	95.31	5.8	5.5	60.5	1.2941	1.17	0.0085	4.1667	0.2887	11.4
307	92-1-121	12.4611	0.0002	0.0222	0.6583	0.0991	0.0097	0.0985	0	0.0037	165.4	121.4	4.3	3.6	59.6	1.0211	4.83	0.5677	5.6667	1.1547	8.9
359	32-1-150	10.0962	0	0.0158	0.5745	0.1099	0.0066	0.209	0	0.0017	167.1	104.6	5.3	5.3	57.2	1.3895	4	0.41	6	1	12.9
	Mg Fe B Sr																				
480	251-1-263.	12.022	0.0138	0.0001	0.3056	0.1205	0.0051	0.0017	0.0302	0.0011	118.3	112.3	1.5	2.1	53.9	1.4801	3.67	0.3374	1.1667	0.2887	13.9

	SAMPLE	Silicon	Strontium	Sodium	Iron	Magnesium	Manganese	Titanium	Boron	Copper	U.T.S.	P.S.	*A	*L	Hv10	Std. Dev.	Poro	Poro	Mod.#	Std. Dev.	Grain#
	#	%	%	%	%	%	%	%	%	%	MPa	MPa	%	%	kg/mm^2	kg/mm^2	Std. No.	Area %	AFS	AFS	ASTM
	Mg Fe B Na																				
	Mg Ti B Sr																				
338	252-1-137.	12.4994	0.0184	0.0001	0.1745	0.0686	0.0029	0.0957	0.0088	0.0032	138.4	96.2	3.4	3.1	53.7	2.9642	3	0.19	3.6667	0.5774	9.05
411	251-1-194.	11.7176	0.0466	0.0002	0.2658	0.1038	0.0034	0.0208	0.1438	0.0081	115.4	73.44	2.2	1.9	49.9	1.3212	1.5	0.025	1	0	13.9
428	251-1-211.	11.4619	0.0349	0.0002	0.2872	0.0653	0.0045	0.0122	0.0934	0.0013	123.1	97.86	0.9	3.3	50.8	0.5307	1	0	1	0	13.9
449	250-1-232.	12.142	0.053	0.0001	0.2896	0.0876	0.0053	0.2433	0.0751	0.0012	129	89.75	1.6	3.2	53.8	2.5967	3.17	0.2274	3.6667	0.5774	10.15
451	253-1-234.	12.3437	0.0237	0.0001	0.2868	0.1026	0.0048	0.2331	0.0736	0.0012	128.9	99.31	3.8	2	55.5	2.0763	5.67	0.9149	1.8333	1.0408	8.9
474	251-1-257.	11.9462	0.046	0.0003	0.2884	0.1072	0.0046	0.0182	0.0675	0.0011	123.4	105.9	0.9	3.1	53.3	1.2853	4.5	0.505	1.1667	0.2887	13.9
	Mg Ti B	No Mod.																			
375	258-1-158.	12.1786	0	0.0001	0.2791	0.0012	0.4725	0.118	0.0163	0.0031	119	114	1.3	2.6	51.8	2.5517	4.17	0.4423	1	0	10.8
	Mg Ti B Na																				
	Mn Fe Ti Sr																				
150	166-2-55	11.4918	0.0296	0.0014	0.6366	0.0014	0.1995	0.2206	0.0003	0.001	148.3	77	3.9	4.6	51.9	0.9893	1.33	0.0165	4.3333	1.2583	11.15
172	162-2-64	11.3572	0.0261	0.0005	0.5751	0.0016	0.1924	0.1088	0	0.0009	163.6	79.14	9	7.4	52.7	0.8672	1	0	4.1667	0.7638	7.8
194	52-2-74	9.7779	0.0311	0.0008	0.5804	0.0017	0.1988	0.1116	0	0.0008	151.8	88.18	8	7	48.8	0.5636	1.33	0.0165	4.3333	1.1547	8.3
195	54-3-74	9.69	0.0268	0.0007	0.5828	0.0012	0.4601	0.1101	0	0.0008	148.1	103.6	12.6	6.9	48.7	1.2956	1.17	0.0085	5	0	8.3
206	64-2-78	10.2572	0.0303	0.0012	0.6039	0.0015	0.1888	0.197	0	0.003	157.7	74.15	6	5.2	53.9	1.6798	1.17	0.0085	4.5	1.3229	12.3
207	66-3-78	10.0807	0.028	0.0011	0.6085	0.0009	0.4764	0.1935	0	0.0029	151.2	86.18	6.6	5.9	50.5	2.197	1	0	5	0	11.8
240	124-2-89	13.2408	0.0311	0.0009	0.6669	0.0019	0.2113	0.1053	0	0.004	150.3	130.8	3	3	54.7	1.8174	1	0	4	1	8.4
241	126-3-89	12.9453	0.0287	0.0006	0.6749	0.0016	0.4629	0.1003	0	0.004	132	76.16	1.6	2.4	53.2	1.5659	1.17	0.0085	4.3333	1.1547	8.2
252	136-2-94	13.1208	0.0288	0.0007	0.7063	0.0028	0.2049	0.2431	0	0.0041	149.2	102	2	2.5	55.8	2.1852	1	0	4.3333	1.1547	10.9
253	138-3-94	13.2453	0.0282	0.0006	0.6886	0.0024	0.4848	0.2393	0	0.0042	131.2	101.5	1.6	2.8	52.6	1.189	1.17	0.0085	4.5	0.5	10.4
277	52-1-106	10.3672	0.0251	0.0007	0.6218	0.0021	0.1924	0.1096	0	0.0028	152.2	122.5	6.7	5.6	50.6	1.1161	1.17	0.0085	4.5	0.866	8.55
	Mn Fe Ti Na																				
148	150-2-54	11.4379	0.0002	0.0112	0.5545	0.0016	0.192	0.0965	0	0.0001	183.2	78.8	14.6	11	54.2	2.95	1.17	0.0085	4.5	2.5981	7.8
162	28-2-60	9.8783	0	0.0068	0.5795	0.0008	0.1937	0.1899	0	0.0009	167.9	99.4	7.2	6.9	54.1	1.0647	1	0	4.6667	1.0408	10.3
163	30-3-60	9.9288	0	0.0104	0.5861	0.0005	0.4837	0.1855	0	0.0009	160	70.56	7.7	8.3	53	1.1548	1.17	0.0085	4.3333	1.1547	9.3
182	18-2-69	10.1296	0	0.0142	0.4503	0.0015	0.4729	0.1015	0	0.0009	158.4	89.19	11.6	9.7	50.4	0.6653	1.5	0.025	4.6667	0.5774	7.55
216	88-2-81	13.1022	0	0.0123	0.6357	0.0024	0.1915	0.1124	0.0003	0.0033	182.7	124.6	2.8	4.1	57.9	3.2352	1.17	0.0085	4	0.5	8.4
217	90-3-81	12.9599	0.0001	0.0127	0.6165	0.0011	0.4504	0.1015	0	0.004	163.4	124.1	3.4	4.7	57.4	2.8442	2.33	0.0962	6.3333	1.1547	7.8
228	100-2-85	12.913	0.0004	0.0154	0.5925	0.001	0.2058	0.1951	0	0.0038	157.8	86.39	7.3	5	57.4	1.6083	1.17	0.0085	7	0	10.15
229	102-3-85	12.8926	0.0004	0.0152	0.5901	0.0005	0.5052	0.1913	0	0.0039	145.1	92.2	4.2	4.5	54.6	2.4114	1.83	0.0415	6.6667	0.5774	10.15
272	18-2-103	10.3299	0	0.0089	0.6157	0.0011	0.48	0.0997	0	0.0027	166.9	110.1	9.4	7.2	54.2	0.7554	2	0.05	4.3333	0.7638	7.8
273	16-1-104	10.3925	0.0001	0.02	0.6197	0.0009	0.2001	0.1005	0	0.0026	165	120.5	5.9	6.5	53.4	0.9566	2	0.05	6	0.866	9.8
305	154-1-120	11.5138	0	0.0211	0.5353	0.001	0.1722	0.1913	0	0.0031	170.6	123.6	6.6	7.4	56.4	1.3952	1.67	0.0335	7	0	12.15
357	28-1-148	10.0154	0	0.0084	0.6633	0.0006	0.1498	0.1796	0.0001	0.0015	154.8	108.7	5.6	4.3	52.6	1.1623	4.33	0.4727	5.3333	0.2887	11.9
	Fe Mn B Sr																				
414	263-1-197.	11.4136	0.0176	0.0001	0.6484	0.0018	0.5159	0.0038	0.0514	0.0012	125.3	78.32	1.8	1.8	52.2	0.6765	1	0	1.5	0	13.15
	Fe Mn B Na																				
	Mn Ti B Sr																				
347	255-1-141.	12.3495	0.0261	0.0001	0.2728	0.0015	0.192	0.0906	0.0083	0.0014	129.3	104	3.6	3.7	50.1	1.1583	2	0.05	3.8333	0.7638	9.4
348	258-2-141.	12.2444	0.0658	0.0001	0.2848	0.0018	0.5161	0.0856	0.0072	0.0016	143.4	102	2.2	5.2	49.8	2.3178	3	0.19	4	1	8.3
366	258-2-154.	12.2814	0.0639	0.0002	0.2834	0.0015	0.5666	0.0858	0.006	0.0014	130.5	99.3	3.3	4.3	48.8	1.3624	1.67	0.0335	4	0.5	9.55

	SAMPLE	Silicon	Strontium	Sodium	Iron	Magnesium	Manganese	Titanium	Boron	Copper	U.T.S.	P.S.	*A	*L	Hv10	Std. Dev.	Poro	Poro	Mod.#	Std. Dev.	Grain#
	#	%	%	%	%	%	%	%	%	%	MPa	MPa	%	%	kg/mm^2	kg/mm^2	Std. No.	Area %	AFS	AFS	ASTM
387	258-1-170.	12.1855	0.0152	0.0001	0.2726	0.002	0.4595	0.0809	0.0036	0.0014	146.9	70.02	9.7	6.1	51.6	1.1243	3.5	0.3	4.6667	0.5774	8.8
413	257-1-196.	11.5217	0.0336	0.0001	0.2415	0.0023	0.5249	0.0147	0.0777	0.0015	121.2	71.49	1.6	2.4	52.3	1.6021	1.33	0.0165	1.6667	0.5774	13.15
475	256-1-258.	12.2677	0.0798	0.0001	0.2875	0.0028	0.2061	0.2716	0.0919	0.0011	135.8	97.05	3.9	4	49.5	1.5476	1.67	0.0335	4.5	0.866	10.3
476	259-1-259.	12.1531	0.0713	0.0001	0.2852	0.0018	0.5048	0.3439	0.1083	0.001	149.1	112.6	8.9	6.5	50.7	1.5371	4.83	0.5677	5	0.5	9.3
	Mn Ti B Na																				
	Fe Ti B Sr																				
341	261-1-138.	12.3184	0.0303	0.0001	0.6446	0.0038	0.0085	0.0861	0.0059	0.0033	121.7	116.3	2.2	3.2	52.6	1.1764	1.17	0.0085	4.1667	1.4434	7.8
421	285-1-204.	11.9534	0.0235	0.0001	0.3028	0.0014	0.0037	0.0215	0.0105	0.0026	141.7	74.91	6.7	3.4	48.7	1.306	1.33	0.0165	4.1667	0.2887	9.3
429	260-1-212.	11.6024	0.0414	0.0002	0.5927	0.0051	0.0052	0.0182	0.0974	0.0012	119.5	91.6	1.3	2.7	49.5	2.5843	1.33	0.0165	1.5	0.5	13.15
430	267-1-213.	11.7047	0.0247	0.0001	0.297	0.0016	0.0038	0.0103	0.0298	0.001	113.2	87.86	2	1.8	49	0.5879	1.17	0.0085	2	0	12.4
448	240-1-231.	12.2784	0.0538	0.0008	0.2974	0.0022	0.0047	0.1424	0.029	0.0013	131.2	82.37	3.9	3.3	51.1	0.3371	3.83	0.3726	3.8333	1.6073	8.8
455	260-1-238.	11.6959	0.0357	0.0001	0.603	0.002	0.0116	0.0129	0.0595	0.0014	114.9	108.3	1.6	2.2	49.5	0.8976	2.5	0.12	1.8333	0.2887	12.15
457	262-1-240.	12.0961	0.0332	0.0001	0.6413	0.0029	0.0179	0.2271	0.0721	0.0016	138.8	88.14	3.4	3.7	50.9	1.1639	3.83	0.3726	4.5	0.5	7.8
464	282-1-247.	12.5816	0.0258	0.0001	0.3095	0.0026	0.017	0.0237	0.0126	0.0012	150.6	94.01	7.6	7.2	49	1.1057	4.33	0.4727	4	0.866	8.15
465	284-1-248.	12.3024	0.0413	0.0001	0.2952	0.0019	0.0056	0.1535	0.0462	0.0014	127.5	91.57	2.7	5	48.7	1.1827	4.83	0.5677	4	0.5	8.3
466	283-1-249.	12.3835	0.0369	0.0002	0.2961	0.0021	0.0052	0.1827	0.0736	0.0013	150.2	83.61	8.1	6.7	48.7	0.4579	3.83	0.3726	4.1667	0.7638	9.3
467	286-1-250.	12.4374	0.0366	0.0002	0.3016	0.0021	0.0055	0.0331	0.0261	0.0013	123.3	107.4	2.6	3	47.1	1.0534	4.17	0.4423	3.8333	1.0408	12.4
468	287-1-251.	12.4548	0.0316	0	0.2996	0.0021	0.0048	0.0964	0.0446	0.0012	137	77.22	4.7	5.8	50.4	1.6654	1.67	0.0335	4.1667	0.7638	10.65
473	237-1-256.	12.3699	0.0114	0.0001	0.2979	0.0019	0.009	0.1692	0.0533	0.0011	115.1	111.9	2.2	2.2	49	0.7874	5.67	0.9149	2	0.866	9.9
483	275-1-266.	12.0471	0.0164	0	0.2981	0.0017	0.0163	0.104	0.0129	0.0011	146.1	128.9	6.3	6.2	51.9	0.9459	1	0	4	1	9.3
484	276-1-267.	12.1696	0.0177	0	0.2978	0.0017	0.0049	0.0874	0.0166	0.0011	137.9	107.7	6.2	5.6	51.8	2.1665	1	0	4.3333	1.1547	9.8
	Fe Ti B Na																				
	Mn Fe Mg Ti Sr																				
110	144-4-38	13.2564	0.0295	0.0029	0.806	0.1104	0.4817	0.1685	0	0.0013	132.3	92.8	3.4	2.6	59.6	2.5248	3.5	0.3	3.3333	1.1547	8.7
145	164-1-53	11.2806	0.0308	0.0024	0.6074	0.1109	0.1909	0.0986	0	0.0013	145.3	74.4	3.4	3.9	53.1	1.9246	1.83	0.0415	4.6667	2.3094	7.8
146	168-2-53	11.3413	0.0269	0.0015	0.5612	0.1022	0.1783	0.1841	0	0.001	144.8	91.4	2.1	2.5	55	4.4823	1	0	4.6667	0.5774	9.8
166	70-2-61	10.1904	0.0296	0.0004	0.5735	0.1284	0.0404	0.2014	0	0.0009	146.2	80.3	3.7	3.4	57.7	0.6976	1.17	0.0085	4.1667	0.2887	10.9
196	60-4-74	9.8624	0.0329	0.0007	0.5723	0.1176	0.4532	0.1085	0	0.0008	135.4	89.8	3.4	2.7	56.1	0.9331	3	0.19	3	0.5	7.55
208	72-4-78	10.3444	0.0274	0.002	0.5938	0.1032	0.4637	0.1948	0	0.003	136.9	86.99	4.1	3.2	55.8	2.0314	1.5	0.025	4	0.866	10.55
238	130-2-88	13.1919	0.0247	0.0007	0.616	0.1019	0.2055	0.1068	0	0.0041	144.7	81.5	1.8	2.3	58.9	2.4417	1.33	0.0165	3.6667	0.5774	8.3
242	132-4-89	13.0173	0.0305	0.0005	0.6535	0.0922	0.4557	0.099	0	0.0041	145	104.5	2.3	2.1	57.2	3.4221	1.33	0.0165	4.3333	0.7638	8.3
250	142-2-93	13.1812	0.0377	0.0007	0.6327	0.1461	0.2006	0.2011	0	0.0042	134	123.2	0	1.2	59.4	2.794	2.67	0.1438	3.3333	0.5774	10.15
254	144-4-94	13.1994	0.032	0.0004	0.6721	0.1158	0.4732	0.2333	0	0.0043	127	88.19	1.4	1.3	59.2	1.8239	1.17	0.0085	3.5	0	10.3
267	197-1-101	11.9594	0.0289	0.0004	0.6204	0.105	0.4918	0.1944	0	0.0035	142.18	103.6	2.1	1.8	56.5	2.4345	2.83	0.1662	2.8333	1.893	11.9
268	198-2-101	11.7018	0.0262	0.0003	0.6158	0.1228	0.4929	0.1914	0	0.0033	142.4	105	2.1	1.9	56.8	1.205	4.67	0.5373	4	1.3229	11.15
276	58-2-105	10.5544	0.0282	0.0008	0.5862	0.1123	0.1959	0.1321	0	0.0033	152.2	104.9	3.1	3.3	57	1.1911	2.67	0.1438	4	0.866	10.8
278	70-2-106	10.3635	0.0253	0.0006	0.597	0.1091	0.1869	0.1981	0	0.0028	150.7	112.8	2.5	2.9	57.2	1.9498	1	0	4.6667	0.5774	12.65
282	58-2-108	10.6758	0.0264	0.0006	0.56	0.1113	0.2002	0.1033	0	0.003	147.8	108.9	0.2	3.6	57.3	0.9381	2.83	0.1662	3	0.5	8.05
299	192-1-117	11.3098	0.0053	0.0001	0.5837	0.1072	0.5145	0.1951	0	0.0031	137.4	112.9	0.4	1.4	58.3	0.9913	2	0.05	2	0.5	11.4
300	193-2-117	11.5901	0.0132	0	0.5779	0.1475	0.5112	0.1958	0	0.0032	140.7	118.3	1.3	2.3	58.4	2.1276	3	0.19	3	1.3229	10.4
301	194-1-118	11.5545	0.0212	0.0002	0.6599	0.1075	0.5351	0.1998	0	0.0032	146.7	118.3	1.1	2.8	57.6	0.9203	5	0.6	3.5	0.866	11.9
302	195-2-118	11.6047	0.0424	0.0002	0.6411	0.1496	0.5235	0.1973	0	0.0032	120	90.83	1.3	1.6	57.6	2.1676	4.67	0.5373	4.1667	1.893	10.65
303	197-1-119	11.6404	0.046	0.0003	0.7311	0.1087	0.5	0.1995	0	0.0032	136.6	129.2	1.1	2.4	57.1	3.946	4.67	0.5373	3.3333	1.5275	11.15
304	198-2-119	11.1964	0.0951	0.0001	0.7099	0.1494	0.4877	0.1908	0	0.0032	123.2	91.62	1.4	1.7	60.4	2.7203	5.67	0.9149	3.1667	1.0408	10.9
314	60-2-124	10.4522	0.0459	0.0002	0.6218	0.1072	0.5144	0.1066	0	0.0032	130.6	83.32	3.3	2.6	57.5	0.9913	6	1.07	3	1	7.55
315	195-1-125	11.5599	0.0274	0.0008	0.7132	0.1097	0.5821	0.2023	0	0.0033	138.7	101.2	1.6	2	59.6	3.4967	4	0.41	3.8333	0.2887	11.8

	SAMPLE	Silicon	Strontium	Sodium	Iron	Magnesium	Manganese	Titanium	Boron	Copper	U.T.S.	P.S.	*A	*L	Hv10	Std. Dev.	Poro	Poro	Mod.#	Std. Dev.	Grain#
	#	%	%	%	%	%	%	%	%	%	MPa	MPa	%	%	kg/mm^2	kg/mm^2	Std. No.	Area %	AFS	AFS	ASTM
316	198-2-125	11.6009	0.0504	0.0007	0.7032	0.1284	0.5734	0.1982	0	0.0034	137.4	98.65	2.5	2.4	58.4	3.3493	5.33	0.7551	3.3333	1.1547	10.3
317	184-1-126	11.2696	0.0001	0.0005	0.6315	0.1095	0.5361	0.2057	0	0.0032	116.3	90.97	0	0.9	61.7	1.9055	1	0	1	0	11.55
322	164-2-128	11.7323	0.0258	0.0002	0.6395	0.1102	0.1767	0.1241	0	0.0032	132.3	96.7	2.3	2.8	58.9	0.7167	3	0.19	3.8333	0.7638	8.8
326	60-2-130	10.3455	0.0262	0.0004	0.6964	0.1145	0.2216	0.1238	0	0.0029	138.9	111.5	0.9	2.4	57.4	1.2044	3.33	0.2626	2.8333	0.2887	10.5
334	60-2-134	10.262	0.0436	0.0001	0.6911	0.1168	0.5255	0.1008	0	0.003	137.5	106.1	3.1	2	53	2.3588	4.83	0.5677	3.5	1.8028	7.55
350	278-2-142.	12.7241	0.0619	0.0008	0.7531	0.1221	0.5125	0.179	0.0007	0.0018	138.2	128	0.7	2.3	60.4	0.8532	4	0.41	2.6667	0.5774	9.9
358	60-1-149	9.8951	0.02	0.0003	0.6806	0.1103	0.5208	0.1012	0	0.0017	138.5	110.4	2.2	3.4	57	2.2737	5	0.6	4.3333	0.5774	8.3
487	RM10	11.4732	0.0166	0.0016	0.4085	0.0948	0.2965	0.1127	0	0.0153	129	98.86	6.5	3.9	56.9	1.7037	4.33	0.4727	3.3333	0.5774	7.8
488	RM11	11.5736	0.0121	0.0025	0.4353	0.0743	0.2919	0.1149	0	0.0034	156.5	121.8	6.9	6.3	51.9	1.2178	5.67	0.9149	4.5	0.5	7.05
491	RMF	12.4608	0.0515	0.0004	0.3707	0.0275	0.1298	0.0391	0.0113	0.0018	148.5	140.6	5.6	6.1	54.1	2.833	1	0	3.5	1	8.3
492	RMG	11.6223	0.0228	0.0003	0.3913	0.0507	0.1395	0.0147	0.0107	0.0392	137.14	120	2.4	4	52.9	4.2283	1.67	0.0335	3.6667	0.5774	9.4
493	RMX	11.0426	0.0435	0.0003	0.4278	0.0247	0.2578	0.0803	0.0021	0.2677	138.2	97.99	3.6	3	52.8	6.0767	5	0.6	2.1667	0.2887	7.9
	Mn Fe Mg Ti Na																				
104	24-2-36	10.2308	0.0005	0.0157	0.5803	0.0944	0.5252	0.0875	0	0.0008	147	93.65	5.1	6.6	55	2.1836	4.33	0.4727	5	1	7.55
128	94-2-45	12.7954	0	0.0092	0.6194	0.0949	0.1843	0.0758	0	0.001	165.2	105	4.4	4.7	58	2.184	2.67	0.1438	3.5	0.5	8.3
153	152-1-57	11.2629	0	0.0188	0.5891	0.1151	0.2146	0.1017	0.0003	0.001	178.2	82.56	5.2	5.2	58.3	0.5715	1.5	0.025	5.8333	1.0408	7.8
154	156-2-57	11.4075	0	0.0219	0.5774	0.121	0.2174	0.2088	0.0003	0.001	167.9	91.2	4.8	4.7	61.2	1.4137	2.83	0.1662	5.6667	1.1547	11.9
164	36-4-60	9.9893	0	0.0117	0.5705	0.1515	0.4723	0.1827	0	0.0009	144.4	76.52	4.4	3.9	58.4	2.858	1.83	0.0415	4.6667	1.4434	9.8
176	34-2-66	10.1299	0	0.0185	0.5732	0.1197	0.1896	0.2053	0	0.0008	160.6	125.8	3.6	4	58.7	0.5742	3.67	0.3374	5	0	12.15
180	22-2-68	10.1325	0	0.0074	0.5983	0.1279	0.189	0.1096	0	0.0008	166.2	125.3	4.1	6.2	57.6	2.2695	1.17	0.0085	4	1	7.8
218	96-4-81	13.2426	0	0.0169	0.5985	0.0957	0.4373	0.1004	0	0.0045	159.4	105.4	3.6	4	55.9	2.0144	3.5	0.3	4.3333	0.5774	8.3
220	94-2-82	13.4368	0	0.0082	0.6945	0.1016	0.1852	0.1043	0	0.0037	160.2	125	1.8	2.8	58.9	2.7539	1.67	0.0335	3.5	0.5	8.9
230	108-4-85	13.1037	0.0002	0.0217	0.5641	0.1358	0.4891	0.1852	0	0.0043	128.7	87.22	0.5	1.8	59.4	1.5198	5	0.6	6	1	9.55
232	106-2-86	13.1653	0.0002	0.0126	0.5925	0.0925	0.1931	0.193	0	0.004	161.4	106.6	2.5	3.1	59.5	8.7804	1.17	0.0085	6	1.7321	11.15
269	185-1-102	11.5563	0.0001	0.0137	0.6138	0.1043	0.5125	0.1717	0	0.0034	162.9	119.6	5.2	4.1	60.1	1.6618	2	0.05	4.6667	0.5774	11.9
270	186-2-102	11.625	0.0001	0.0125	0.6241	0.118	0.519	0.1698	0	0.0031	163.6	118.1	4.3	4.3	61.6	1.3992	1.17	0.0085	3.8333	0.7638	10.65
274	22-2-104	10.5863	0.0001	0.0146	0.6092	0.1004	0.1947	0.1007	0	0.0031	154.9	131.3	4.4	3.6	57.1	1.2712	4.33	0.4727	4.3333	1.1547	8.05
291	185-1-113	11.8983	0.0002	0.0041	0.5667	0.1061	0.5087	0.1926	0	0.0033	140.1	96.95	3.8	3.9	56.9	3.7474	1.83	0.0415	2.1667	0.2887	11.4
292	186-2-113	11.9294	0.0004	0.0122	0.5468	0.1143	0.4944	0.1863	0	0.0036	155.2	123.2	3.4	2.3	57.8	2.3847	1.17	0.0085	4	1	10.8
297	189-1-116	11.6816	0.0002	0.0416	0.5928	0.1008	0.5178	0.1893	0	0.0033	141.2	135	3.5	5.6	57	1.7759	5	0.6	6.6667	0.5774	11.65
298	190-2-116	11.5151	0.0003	0.0668	0.5527	0.1023	0.4932	0.1785	0	0.0036	145	129	3.6	5.5	55.6	1.0477	5.17	0.6799	8	0	10.8
306	191-2-120	11.6252	0.0001	0.0567	0.4805	0.1103	0.4238	0.1753	0	0.0034	140.4	122.8	2.9	3.7	56.8	1.4292	6	1.07	7	0	10.8
308	108-2-121	12.814	0.0001	0.0132	0.6689	0.1058	0.5194	0.2056	0	0.0041	154.6	99.24	2	1.9	59.4	1.7291	1.17	0.0085	4.1667	0.2887	10.8
318	189-2-126	11.7104	0.0005	0.034	0.5891	0.1163	0.5156	0.1887	0	0.0035	147.3	105.6	4.1	4.7	58.4	1.7108	1.17	0.0085	7.6667	0.5774	11.15
	Mg Mn Fe B Sr																				
416	273-1-199.	11.3811	0.0226	0.0001	0.6683	0.0977	0.5175	0.008	0.0615	0.0013	129.1	88.59	4.7	1.9	54.2	1.1179	1.5	0.025	1	0	13.4
422	270-1-205.	11.8333	0.0177	0.0001	0.7695	0.1077	0.5575	0.0075	0.0058	0.0021	136.2	123.3	1.6	3	57.8	2.1606	1.17	0.0085	2.8333	1.0408	8.3
423	271-1-206.	11.8145	0.022	0.0001	0.8104	0.1053	0.5319	0.0034	0.0189	0.0021	128.2	113.2	2.2	0.9	56.2	2.1229	5	0.6	2	1	11.9
436	272-1-219.	11.6264	0.0131	0	0.666	0.1031	0.5031	0.0021	0.0338	0.0014	129.9	105.5	0.7	1.4	56.3	3.4994	4.67	0.5373	1	0	14.4
	Mg Mn Fe	B Na																			
	Mg Mn Ti B Sr																				
381	293-1-164.	12.1686	0.0231	0	0.2637	0.1045	0.5181	0.0706	0.0034	0.0015	140.2	85.6	2	3	57.2	1.5368	5	0.6	3.6667	1.0408	9.8
469	293-1-252.	12.4273	0.0281	0.0001	0.2926	0.0996	0.5248	0.1431	0.0288	0.0012	146.2	109.9	2	3	53.9	1.5329	5	0.6	2.6667	0.5774	9.55
	Mg Mn Ti B Na																				

	SAMPLE	Silicon	Strontium	Sodium	Iron	Magnesium	Manganese	Titanium	Boron	Copper	U.T.S.	P.S.	*A	*L	Hv10	Std. Dev.	Poro	Poro	Mod.#	Std. Dev.	Grain#
	#	%	%	%	%	%	%	%	%	%	MPa	MPa	%	%	kg/mm^2	kg/mm^2	Std. No.	Area %	AFS	AFS	ASTM
	Mg Fe Ti B Sr																				
379	292-1-162.	12.1928	0.0228	0.0002	0.7515	0.1058	0.0123	0.0804	0.0053	0.0038	131.5	88.8	1.5	2.8	54.9	3.5275	6	1.07	1.8333	0.2887	9.4
433	289-1-216.	12.364	0.0261	0.0001	0.5371	0.1105	0.0207	0.0628	0.0038	0.0019	149.1	76.7	1.3	2.5	58.3	1.6327	1	0	3.5	0.5	7.8
471	292-1-254.	12.3964	0.0312	0.0001	0.6487	0.1086	0.0145	0.1522	0.0287	0.0013	131.6	122	1.5	2	56	2.1797	5.5	0.835	2.3333	1.4434	9.05
	Mg Fe Ti	B Na																			
	Mn Fe Ti B Sr																				
342	264-2-138.	12.3108	0.0577	0.0003	0.6598	0.0042	0.5583	0.0847	0.0064	0.0035	141	97.8	3.9	3.9	53	0.7333	3.33	0.2626	3.1667	3.1667	8.3
383	291-1-166.	12.0606	0.0254	0.0005	0.7329	0.0017	0.5252	0.0741	0.0041	0.0142	136.8	77.2	4	3.2	52.3	2.1056	6	1.07	4.3333	0.5774	7.8
438	258-1-221.	12.1865	0.0233	0.0005	0.3031	0.0049	0.4942	0.0998	0.0154	0.0037	149.9	100.3	9	6.5	52.6	1.5582	6	1.07	4.1667	0.7638	9.8
452	256-1-235.	12.2983	0.0367	0.0002	0.2965	0.0028	0.1766	0.2039	0.0644	0.0012	143.6	77.18	5.3	5.3	50.6	0.973	3.17	0.2274	4	1	8.55
454	259-1-237.	12.1276	0.0352	0.0001	0.2997	0.0027	0.51	0.1595	0.0482	0.002	147.9	108.5	7.2	5.1	50	0.8849	5	0.6	4.1667	0.5774	7.55
470	291-1-253.	12.249	0.0407	0.0001	0.6677	0.0029	0.5642	0.1976	0.0438	0.0013	144.1	108.7	2	4.4	52.5	1.675	1.17	0.0085	4.6667	0.2887	8.8
477	260-1-260.	11.6997	0.0135	0.0001	0.5852	0.0017	0.0291	0.0165	0.048	0.001	116.1	102.3	1.4	1.4	49.7	1.8929	1.67	0.0335	1.3333	0.2887	13.65
481	256-1-264.	12.0414	0.0175	0	0.3059	0.0031	0.2412	0.071	0.0199	0.0012	148.1	109.1	8.5	6.6	52.6	1.2189	1	0	4	0.866	9.55
482	259-1-265.	12.1277	0.0176	0.0002	0.3038	0.0032	0.5466	0.0705	0.0174	0.001	154.3	98.77	10.3	7.8	50.5	1.4892	3.33	0.2626	4.1667	1.0408	9.3
	Mn Fe Ti B Na																				
	Mg Mn Fe Ti B Sr																				
330	289-2-132.	12.7696	0.0298	0.0005	0.734	0.1132	0.5693	0.111	0.0113	0.0041	138.8	117	2.5	3.1	62.1	2.9791	2	0.05	3	1	10.15
340	289-2-137.	12.4328	0.0639	0.0001	0.4626	0.1661	0.4618	0.0893	0.008	0.0034	140.7	116.5	2.3	2.5	57	1.8417	1.5	0.025	2	1.7321	7.55
352	279-2-143.	12.2637	0.0547	0.0002	0.5941	0.1101	0.487	0.1948	0.0146	0.0017	135.5	87.1	0.5	2.6	56.1	1.1179	2.5	0.12	2.1667	0.7638	11.4
354	280-2-144.	12.1541	0.0626	0.0001	0.6463	0.113	0.4749	0.1948	0.0254	0.0019	148.2	110	2.6	2.6	58	2.9717	2	0.05	2.8333	1.0408	8.65
356	264-2-146.	12.0967	0.0409	0	0.7092	0.1083	0.5027	0.0866	0.008	0.0016	140.9	119	2.5	2.7	56.9	5.084	1.67	0.0335	3	1	8.05
370	278-2-155.	12.48	0.0429	0.0001	0.6306	0.1209	0.4001	0.1832	0.0029	0.0017	133.9	130	0.5	2.5	58.6	1.9826	4.33	0.4727	2.5	1.3229	11.9
373	279-2-156.	12.0191	0.0641	0.0001	0.6454	0.1184	0.5275	0.2481	0.0462	0.0016	129.8	118	2.1	1.6	57.9	1.5531	4.83	0.5677	2	1	8.3
376	264-1-159.	12.1161	0.0239	0.0001	0.7629	0.1069	0.4935	0.0983	0.0123	0.0044	129	109.7	4.8	2.9	56.4	1.5735	6	1.07	2.5	0	9.3
378	279-1-161.	12.1789	0.0255	0.0001	0.7244	0.1076	0.5172	0.2114	0.0358	0.0033	136.3	82.4	3.8	2.7	57	1.8422	6	1.07	1.8333	0.2887	9.4
380	289-1-163.	12.8207	0.0256	0	0.3819	0.1097	0.5485	0.078	0.0051	0.0025	136.3	88.3	2.4	2.6	54.8	1.8129	5.33	0.7551	2.1667	1.2583	9.55
382	278-1-165.	12.1169	0.0228	0.0001	0.733	0.0969	0.4943	0.1958	0.0089	0.0018	136.7	87.9	2.7	2.3	56.2	2.9786	6.83	1.4352	3.1667	0.7638	11.9
393	278-1-176.	12.2254	0.0219	0.0002	0.6795	0.1002	0.5002	0.242	0.0044	0.0027	133.5	110.2	1.5	2.2	57	1.9572	5	0.6	2.1667	1.0408	12.15
478	281-1-261.	12.0017	0.0205	0	0.5493	0.1039	0.5586	0.1458	0.0485	0.001	137.8	101.9	2.6	1.6	54.5	1.6395	5.5	0.835	2.5	0.866	7.8
485	279-1-268.	12.0135	0.018	0	0.652	0.105	0.5321	0.1192	0.0179	0.0017	132.6	114.1	1.5	1.5	57.6	2.0963	4	0.41	2.6667	1.2583	10.3
494	RMY	12.0611	0.0207	0.0006	0.2226	0.014	0.0872	0.0511	0.0086	0.0049	142.4	101.8	4.7	5	50.3	1.8284	1.33	0.0165	4	0.866	7.9
453	289-1-236.	12.7557	0.0299	0.0007	0.7063	0.1027	0.523	0.0941	0.015	0.002	133.8	94.49	4	2.4	59.7	3.8573	5.5	0.835	1.6667	1.1547	9.4
456	281-1-239.	11.9546	0.033	0.0002	0.5975	0.1158	0.471	0.5321	0.1477	0.0013	137.7	80.92	2	2	53.4	2.223	6	1.07	3.1667	0.2887	8.3
458	265-1-241.	12.1092	0.0295	0.0003	0.6096	0.1079	0.5233	0.1474	0.0437	0.0015	132.4	108.3	2.7	1.7	55.3	1.7781	5.5	0.835	1.6667	0.5774	8.8
462	279-1-245.	12.1016	0.0304	0.0002	0.6282	0.0513	0.5028	0.2471	0.0523	0.0013	148.4	106.1	3.7	3.8	54.4	1.9142	5.17	0.6799	4	1	9.4
463	280-1-246.	12.314	0.0321	0.0001	0.6704	0.0775	0.5213	0.182	0.0521	0.0013	138.8	106.8	2.9	2.9	56.6	3.4126	4.67	0.5373	3	0	9.55
	Mg Mn Fe Ti B Na																				
328	288-2-131.	12.8581	0.0001	0.0098	0.6312	0.0964	0.515	0.1311	0.017	0.004	155.2	110	2.9	3.6	59.7	1.359	1.5	0.025	3.1667	0.2887	8.65

Appendix O

Main MLR Anaylsis Outputs

Appendix O Part 1-The Modification MLR Results

Sodium Modified Samples

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.951761736					
R Square	0.905850402					
Adjusted R Square	0.904138591					
Standard Error	0.590652801					
Observations	225					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	4	738.4570308	184.6142577	529.176686	1.3268E-111	
Residual	220	76.75156096	0.348870732			
Total	224	815.2085917				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.348226244	0.100746368	3.4564645	0.00065678	0.149674616	0.546777872
n^5 Na Spline	83833387.91	2371551.206	35.34960059	1.0962E-92	79159518.65	88507257.17
Mg Na spline	-152876158	15345272.5	-9.962427064	1.5553E-19	-183118725.5	-122633590.6
Titanium	2.831532566	0.481550424	5.880033383	1.5097E-08	1.882489713	3.780575418
Iron	0.965261933	0.214409314	4.501958963	1.0916E-05	0.542702597	1.387821268
$SiB^{0.3}$	0.039832927	0.029126242	1.367595827	0.17283408	-0.017569269	0.097235122
The SiB Term does not appear in the MLR resuls presented in Chapter 8 -this term has very little effect on the recorded R^2 term.						
Note the absence of a copper term						
Na Spline $= Na^5 - 0.1730624 * Na^4 + 0.011192 * Na^3 - 0.0003593 * Na^2 + 0.0000070776 * Na$						

Strontium Modified Samples

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.839306291					
R Square	0.704435051					
Adjusted R Square	0.698190721					
Standard Error	0.677529441					
Observations	291					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	6	310.7153507	51.78589178	112.811953	3.49635E-72	
Residual	284	130.3691046	0.459046143			
Total	290	441.0844553				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	1.227110798	0.156744687	7.82872338	9.8355E-14	0.918582209	1.535639386
n^4 Sr Spline	-731626.588	36472.67251	-20.05958263	2.3346E-56	-803417.6156	-659835.5603
Mg*Sr Spline	1883812.184	224947.3566	8.374457974	2.5728E-15	1441036.791	2326587.577
$SiB^{0.3}$	-0.279223117	0.023144234	-12.06447846	2.4547E-27	-0.324779097	-0.233667136
Titanium	3.879573386	0.483351628	8.026399753	2.673E-14	2.928167643	4.830979128
Sodium	160.9828557	55.27453431	2.912423555	0.00387103	52.1831614	269.7825501
Iron	-0.404172032	0.199220439	-2.028767898	0.04341472	-0.796307817	-0.012036247
Note the absence of a copper term						
Sr Spline $= Sr^4 - 0.20533 * Sr^3 + 0.01432 * Sr^2 - 0.0004062 * Sr$						

The Full Observation Set

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.89955456					
R Square	0.809198406					
Adjusted R Square	0.805256224					
Standard Error	0.705239018					
Observations	495					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	10	1020.918433	102.0918433	205.266644	5.1008E-167	
Residual	484	240.7232431	0.497362072			
Total	494	1261.641676				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.605459866	0.116054616	5.262369193	2.1408E-07	0.379391709	0.831528022
n^5 Na Spline	90681062.58	2466365.678	36.76707935	3.245E-142	85834957.63	95527167.53
n^4 Sr Spline	-815218.7789	37432.22421	-21.77852896	8.3148E-74	-888768.4916	-741669.0662
MgNa Spline	-210265899.8	19801466.84	-10.61870322	8.0717E-24	-249173344.6	-171358455
Titanium	3.975157323	0.384337324	10.3428865	8.6952E-23	3.219981792	4.730332854
$SiB^{0.3}$	-0.184064758	0.020507834	-8.975338781	6.255E-18	-0.224360127	-0.143769388
MgSr Spline	2116134.614	297807.5142	7.105712626	4.3097E-12	1530979.508	2701289.719
NaSr	-17018.7432	3682.191713	-4.62190579	4.8833E-06	-24253.79664	-9783.689755
Mg*Na@Sr Splines	-1.38805E+14	4.39614E+13	-3.157433905	0.00169101	-2.25184E+14	-5.24264E+13
Manganese	-0.312115588	0.165314327	-1.888012941	0.05962208	-0.636937891	0.012706714
Copper	-4.519465411	2.576073365	-1.754400893	0.07999462	-9.581132461	0.542201639
Na Spline $= Na^6 - 0.1730624 * Na^4 + 0.011192 * Na^3 - 0.0003593 * Na^2 + 0.0000070776 * Na$						
Sr Spline $= Sr^4 - 0.20533 * Sr^3 + 0.01432 * Sr^2 - 0.0004062 * Sr$						

Appendix O Part 2-The Porosity MLR Results

Sodium Modified Samples

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.50042688					
R Square	0.25042706					
Adjusted R Square	0.23686013					
Standard Error	0.24258758					
Observations	226					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	4	4.345069803	1.08626745	18.458637	4.21111E-13	
Residual	221	13.00557052	0.05884874			
Total	225	17.35064033				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.20976241	0.147647689	1.4206955	0.1568146	-0.08121528	0.50074009
$Na^{1.57}$	57.138357	9.285126812	6.15375085	3.516E-09	38.83963034	75.4370837
$B^{+A89.5}$	1.26308227	0.234309495	5.39065764	1.797E-07	0.801315242	1.7248493
Magnesium	0.89646127	0.355337306	2.52284592	0.0123447	0.196177866	1.59674468
Silicon	-0.0160988	0.012841473	-1.2536583	0.2112908	-0.04140624	0.0092086

Strontium Modified Samples

Regression Statistics						
Multiple R	0.46923328					
R Square	0.22017987					
Adjusted R Square	0.20664133					
Standard Error	0.27871402					
Observations	294					
Analysis of Variance						
	df	*Sum of Squares*	*Mean Square*	*F*	*Significance F*	
Regression	5	6.316744334	1.26334887	16.263187	3.95106E-14	
Residual	288	22.37227393	0.07768151			
Total	293	28.68901826				
	Coefficients	*Standard Error*	*t Statistic*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.07063867	0.038968512	1.81271143	0.0708997	-0.00606062	0.14733795
$B^{0.2}$	0.37203881	0.083800719	4.43956578	1.278E-05	0.207099089	0.53697852
Magnesium	1.41694459	0.346346942	4.09111333	5.554E-05	0.735251556	2.09863762
Manganese	0.24406528	0.081404767	2.99816937	0.0029489	0.083841365	0.40428919
Sodium	-67.110129	22.7225978	-2.9534532	0.003397	-111.833597	-22.38666
Copper	1.11262749	1.022274149	1.08838465	0.2773198	-0.89945081	3.12470579

The Full Observation Set

Regression Statistics						
Multiple R	0.44391903					
R Square	0.1970641					
Adjusted R Square	0.18885413					
Standard Error	0.26726897					
Observations	495					
Analysis of Variance						
	df	*Sum of Squares*	*Mean Square*	*F*	*Significance F*	
Regression	5	8.572995366	1.71459907	24.002999	1.28604E-21	
Residual	489	34.93059143	0.0714327			
Total	494	43.5035868				
	Coefficients	*Standard Error*	*t Statistic*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.01170385	0.022767482	0.51405985	0.60744	-0.03303031	0.05643801
$B^{0.27}$	0.63446658	0.072549112	8.74533903	3.505E-17	0.491920133	0.77701302
Magnesium	1.31311688	0.260313532	5.04436656	6.403E-07	0.801645851	1.8245879
Na^2	175.29574	33.40888016	5.24698041	2.299E-07	109.6530739	240.938405
Manganese	0.13238774	0.061382996	2.15674939	0.031507	0.011780779	0.2529947
Copper	1.3598175	0.973886442	1.39628075	0.1632571	-0.5536988	3.27333379

The Al-3%B Refined Samples

Regression Statistics						
Multiple R	0.41570792					
R Square	0.17281308					
Adjusted R Square	0.16157412					
Standard Error	0.23377335					
Observations	374					
Analysis of Variance						
	df	*Sum of Squares*	*Mean Square*	*F*	*Significance F*	
Regression	5	4.201561998	0.8403124	15.376262	9.77644E-14	
Residual	368	20.11119297	0.05464998			
Total	373	24.31275497				
	Coefficients	*Standard Error*	*t Statistic*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.0501188	0.023351648	2.14626407	0.0324965	0.004199372	0.09603824
Na^2	190.885186	30.41387838	6.2762527	9.635E-10	131.0783583	250.692014
$B^{0.27}$	0.4799047	0.095832813	5.00772841	8.514E-07	0.291455976	0.66835342
Magnesium	1.06439643	0.249092874	4.27309065	2.45E-05	0.574572197	1.55422066
Manganese	0.02874495	0.061850598	0.46474818	0.642383	-0.09288005	0.15036996
Copper	-2.2400618	4.366082199	-0.5130599	0.6082131	-10.8256661	6.34554256

The Al-5%Ti-1%B Refined Samples

Regression Statistics						
Multiple R	0.47942788					
R Square	0.22985109					
Adjusted R Square	0.22000264					
Standard Error	0.23681714					
Observations	397					
Analysis of Variance						
	df	*Sum of Squares*	*Mean Square*	*F*	*Significance F*	
Regression	5	6.544476106	1.30889522	23.338805	1.56971E-20	
Residual	391	21.92820205	0.05608236			
Total	396	28.47267816				
	Coefficients	*Standard Error*	*t Statistic*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-0.0250789	0.025346945	-0.9894241	0.3230598	-0.07491225	0.02475449
Na^2	186.370626	30.55809892	6.09889466	2.541E-09	126.2918714	246.449381
$B^{0.27}$	0.7338037	0.109818567	6.68196391	8.019E-11	0.517894891	0.94971251
Magnesium	1.12477281	0.245826903	4.5754667	6.367E-06	0.641464789	1.60808083
Copper	23.0908826	7.616665673	3.03162612	0.0025923	8.116135938	38.0656293
Manganese	0.09789695	0.059530291	1.64448969	0.1008687	-0.01914259	0.21493649

Appendix O Part 3-The Vickers Hardness MLR Results

Sodium Modified Samples

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.91624363					
R Square	0.83950239					
Adjusted R Square	0.83358542					
Standard Error	1.45226049					
Observations	226					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	8	2393.878686	299.234836	141.88063	8.30966E-82	
Residual	217	457.6661365	2.10906054			
Total	225	2851.544823				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	15.4717538	2.057327543	7.52031628	1.428E-12	11.41684995	19.5266577
n^2 Si Spline	-0.13709287	0.008801708	-15.575713	3.218E-37	-0.15444066	-0.1197451
Iron	8.14272152	0.593717253	13.7148137	3.043E-31	6.972530423	9.31291262
Magnesium	26.4429666	2.217693282	11.9236356	1.538E-25	22.07198875	30.8139444
Titanium	15.3970186	1.363450693	11.2926846	1.456E-23	12.70971608	18.0843211
Manganese	4.59607454	0.85561866	5.37163897	2.004E-07	2.90968706	6.28246202
(Fe-0.05)*Mn^2	-11.9282832	3.958153326	-3.0135981	0.0028887	-19.7296327	-4.1269337
TiB	-93.6659722	18.54492899	-5.0507593	9.32E-07	-130.217227	-57.114717
Porosity Area	-0.57820163	0.367292747	-1.5742256	0.1168921	-1.3021198	0.14571653
Si Spline = Si^2-31.7*Si						

Strontium Modified Samples

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.92537365					
R Square	0.85631639					
Adjusted R Square	0.85176304					
Standard Error	1.5099935					
Observations	294					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	9	3859.184285	428.798254	188.06278	4.065E-114	
Residual	284	647.5428238	2.28008037			
Total	293	4506.727109				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	22.1689052	2.008463096	11.0377458	8.294E-24	18.21554449	26.1222659
Magnesium	42.1924663	2.00903462	21.0013635	9.554E-60	38.23798066	46.146952
n^2 Si Spline	-0.09478917	0.00773802	-12.249797	5.523E-28	-0.1100203	-0.079558
Iron	7.09737195	0.585525295	12.1213755	1.554E-27	5.94485255	8.24989135
Titanium	10.4088935	1.356014545	7.67609283	2.653E-13	7.739780706	13.0780063
Manganese	6.5446555	0.898099241	7.28722975	3.142E-12	4.776880812	8.3124302
n^2 Sr Spline	847.38438	157.4541918	5.38178355	1.545E-07	537.4592374	1157.30952
(Fe+0.05)*Mn^2	-13.1936256	3.08283065	-4.2797114	2.561E-05	-19.2617189	-7.1255323
TiB	-83.2026214	15.96407712	-5.2118654	3.602E-07	-114.625531	-51.779712
Porosity Area	-0.65201339	0.304760467	-2.139429	0.0332534	-1.25188902	-0.0521378
Sr Spline = Sr^2-0.093*Sr						
Si Spline = Si^2-34.3*Si						

The Full Observation Set

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.91334637					
R Square	0.8342016					
Adjusted R Square	0.83077601					
Standard Error	1.57126986					
Observations	495					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	10	6012.257739	601.225774	243.52078	9.9503E-182	
Residual	484	1194.942261	2.46888897			
Total	494	7207.2				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	18.4579865	1.655543177	11.1492027	7.515E-26	15.20504793	21.710925
Magnesium	36.256931	1.591902218	22.7758531	1.402E-78	33.12903915	39.3848229
n^2 Si Spline	-0.12125101	0.007046866	-17.206375	4.036E-52	-0.13509723	-0.1074048
Iron	7.58621176	0.445851236	17.0151188	3.122E-51	6.710168963	8.46225455
Titanium	13.3514521	1.034626915	12.9046054	5.952E-33	11.31853753	15.3843666
Strontium	-47.0602432	4.469815838	-10.528452	1.764E-23	-55.8428811	-38.277605
Manganese	5.87452035	0.721270079	8.14468883	3.259E-15	4.457313434	7.29172727
TiB	-121.676766	18.37450015	-6.6166026	9.763E-11	-157.680397	-85.473135
$(Fe+0.05)*Mn^2$	-12.3861555	2.528390042	-4.898831	1.317E-06	-17.3541307	-7.4181803
Boron	13.6705569	4.861239318	2.81215467	0.005121	4.11882001	23.2222937
Porosity Area	-0.61171858	0.255759627	-2.3917715	0.017148	-1.11425476	-0.1091824
Si Spline = Si^2-31.8931*Si						

Appendix O Part 4-The Grain Size MLR Results

The Full Observation Set

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.861711555					
R Square	0.742546804					
Adjusted R Square	0.738830984					
Standard Error	0.979250351					
Observations	493					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	7	1341.389044	191.6270063	199.8339364	1.6623E-138	
Residual	485	465.0816559	0.958931249			
Total	492	1806.4707				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.325743677	2.010478913	0.162022926	0.871355276	-3.624581615	4.276068969
B0.5	32.18483299	1.045651066	30.77970658	3.9413E-116	30.13026688	34.23939911
(Ti B)0.45	-67.47883288	2.259583049	-29.8634002	5.8495E-112	-71.91861487	-63.03905089
Titanium	19.7787327	0.68154556	29.02041165	4.3515E-108	18.43958577	21.11787963
n^2 Si Spline	-0.042034555	0.012153971	-3.458503877	0.000591041	-0.065915501	-0.018153609
Manganese	-0.783680897	0.216249668	-3.623963475	0.000320756	-1.208582907	-0.358778887
Sodium	17.35208414	5.843417035	2.969509797	0.003130518	5.870542126	28.83362615
Strontium	-6.926337121	3.367494229	-2.056822269	0.040237621	-13.54301812	-0.309656122
Si Spline = Si^2-26.09*Si						

Samples Not Containing Boron

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.851967069					
R Square	0.725847887					
Adjusted R Square	0.71916125					
Standard Error	0.949368132					
Observations	253					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	6	587.0274702	97.83791169	108.5520115	3.06623E-66	
Residual	246	221.719763	0.90129985			
Total	252	808.7472332				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	7.067544991	0.592935203	11.91959079	3.71033E-26	5.899666435	8.235423548
Titanium	19.08351863	0.78185632	24.40796108	1.16938E-67	17.54353041	20.62350686
Silicon	0.02641662	0.048905463	0.540156822	0.589577548	-0.069910334	0.122743573
Manganese	-1.136416209	0.30404726	-3.737630163	0.000231037	-1.735284809	-0.53754761
Sodium	18.55178587	7.81776678	2.373028819	0.018412235	3.153472313	33.95009943
Strontium	-3.963765784	5.064746738	-0.782618754	0.434603732	-13.93957608	6.012044516
Magnesium	0.997488118	1.1866734	0.840575105	0.40140227	-1.339850616	3.334826852

Sodium Modified Samples

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.865518034					
R Square	0.749121467					
Adjusted R Square	0.742216553					
Standard Error	0.962139147					
Observations	225					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	6	602.5887302	100.431455	108.491068	1.19938E-62	
Residual	218	201.8051587	0.925711737			
Total	224	804.3938889				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	5.002216566	0.593679942	8.425779981	4.85396E-15	3.832128702	6.172304431
Titanium	19.41826153	0.945520192	20.53711988	7.18762E-53	17.55472931	21.28179375
(TiB)0.45	-58.44693804	3.836519989	-15.23436297	3.60387E-36	-66.00836157	-50.88551451
B0.5	28.47633641	1.97461211	14.42123052	1.49655E-33	24.58455988	32.36811295
Silicon	0.210230514	0.051338998	4.094947768	5.95104E-05	0.109046131	0.311414896
Manganese	-1.445116403	0.328604204	-4.397741682	1.71006E-05	-2.092764679	-0.797468127
Sodium	19.20129801	6.662988048	2.88178485	0.004349571	6.069169218	32.3334268
no benefit was found when using a Si spline						

Strontium Modified Samples

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.868846247					
R Square	0.754893801					
Adjusted R Square	0.749751713					
Standard Error	0.972024336					
Observations	293					
ANOVA						
	df	*MS*	*F*	*Significance F*	*SS*	
Regression	6	138.7077166	146.8068587	2.84508E-84	832.2462999	
Residual	286	0.94483131			270.2217547	
Total	292				1102.468055	
	Coefficients	*t Stat*	*P-value*	*Lower 95%*	*Standard Error*	*Upper 95%*
Intercept	6.327463038	9.904325501	4.47702E-20	5.070002829	0.638858551	7.584923248
B0.5	33.5069213	27.49517713	2.80963E-82	31.10826765	1.218647225	35.90557495
(TiB)0.45	-71.65935001	-25.44799459	1.90307E-75	-77.2018901	2.815913441	-66.11680996
Titanium	20.05301094	21.18983248	1.44522E-60	18.19031655	0.946350612	21.91570533
Strontium	-7.057059576	-1.689199364	0.092271049	-15.2800998	4.177754104	1.16598063
Silicon	0.082281712	1.465329486	0.143929513	-0.02824254	0.056152362	0.19280596
Manganese	-0.344977238	-1.28009867	0.201547745	-0.87541757	0.269492693	0.185463089
no benefit was found when using a Si spline						

Appendix O Part 5-The Tensile Test Results

(a) Ultimate Tensile Strength

Sodium Modified Samples

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.858129581					
R Square	0.736386377					
Adjusted R Square	0.725034595					
Standard Error	9.529455925					
Observations	219					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	9	53017.64026	5890.848917	64.86966768	1.16081E-55	
Residual	209	18979.40082	90.81053023			
Total	218	71997.04107				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-243.9745916	69.93474091	-3.488603638	0.000591971	-381.8425263	-106.106657
n^5 Na spline	1.051622217	0.051404737	20.45769075	8.54469E-52	0.950283957	1.15296048
n^2 Si Spline	-2.670868108	0.532708723	-5.013749524	1.13699E-06	-3.721039319	-1.6206969
Iron	20.05758283	4.184055119	4.793814196	3.10399E-06	11.80922113	28.3059445
Magnesium*Na spline	-1.345785534	0.323092637	-4.165324064	4.54808E-05	-1.982723828	-0.70884724
$((Fe+0.325)(Mn+0.05))^2$	-54.34915439	15.7272104	-3.455740275	0.000664573	-85.3534591	-23.3448497
Titanium	15.45897181	8.98677215	1.720191805	0.086877766	-2.25736917	33.1753128
Boron	-97.10739135	38.03211393	-2.553299865	0.011383615	-172.083132	-22.1316506
Manganese	9.708935553	6.41563974	1.513323058	0.131708329	-2.93872696	22.3565981
Strontium	-47.81860746	1966.422832	-0.024317561	0.980622507	-3924.384834	3828.74762
Na Spline $= 1,562,216,460.99*Na^5 - 302,724,433.82*Na^4 + 21,878,711.9*Na^3 - 720,994.1*Na^2 + 10,161.01*Na$						
Si Spline $= Si^2 - 23Si$						

Strontium Modified Samples

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.669950415					
R Square	0.448833559					
Adjusted R Square	0.43086074					
Standard Error	9.406870264					
Observations	286					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	9	19888.49615	2209.832905	24.97290857	3.47788E-31	
Residual	276	24423.02145	88.48920817			
Total	285	44311.5176				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	62.44948141	18.23091325	3.425471919	0.000707075	26.56016511	98.3387977
n^2 Si Spline	-0.501915592	0.184203461	-2.724789152	0.00684522	-0.864537923	-0.13929326
n^3 Sr spline	1.105281206	0.106367171	10.3911874	1.45896E-21	0.895887141	1.31467527
Boron	-140.2382332	23.34350842	-6.007590231	5.9282E-09	-186.1921876	-94.2842787
Titanium	35.41134536	7.156789902	4.947936973	1.30602E-06	21.32251213	49.5001786
Manganese	28.50730799	5.395374733	5.283656724	2.57348E-07	17.88599091	39.1286251
$((Mn+0.05)(Fe+0.325))^2$	-48.94125178	11.33648503	-4.317145185	2.20562E-05	-71.2582192	-26.6242844
Mg*(Sr Spline)	-3.165730931	0.691340814	-4.579117661	7.07211E-06	-4.526702199	-1.80475966
Iron	12.27597745	3.904777464	3.143835356	0.00184939	4.589045284	19.9629096
Sodium	983.70776	763.8401064	1.287845129	0.198878612	-519.9853791	2487.4009
Si Spline $= Si^2 - 20*Si$						
Sr Spline $= 176,630.16*Sr^3 - 30,116.56*Sr^2 + 1,414.5*Sr$						

Unmodified Sample Set

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.919961714					
R Square	0.846329556					
Adjusted R Square	0.788703139					
Standard Error	2.624355553					
Observations	23					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	6	606.8963008	101.1493835	14.68648589	1.04352E-05	
Residual	16	110.1958731	6.887242069			
Total	22	717.0921739				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	148.892033	7.057252881	21.09773244	4.19174E-13	133.9313286	163.852737
iron	-21.02864959	4.006981924	-5.248002109	7.96447E-05	-29.52306989	-12.5342293
$((Fe+0.325)(Mn+0.05))^2$	36.7897375	7.114677595	5.170963407	9.28571E-05	21.70729817	51.8721768
magnesium	116.3912255	25.02039442	4.651854145	0.000265851	63.35037073	169.43208
silicon	-2.712813614	0.63705083	-4.258394287	0.000600576	-4.063300739	-1.36232649
titanium	39.08058369	15.16487437	2.577046321	0.020262892	6.932493418	71.228674
boron	-109.988107	45.6418394	-2.409808818	0.028359912	-206.7444624	-13.2317517
Si Spline was of no significance						

The Full Observation Set

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.822320719					
R Square	0.676211366					
Adjusted R Square	0.66936594					
Standard Error	9.691705931					
Observations	484					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	10	90881.12981	9088.112981	98.78295343	4.3059E-109	
Residual	473	43516.38912	92.00082267			
Total	483	134397.5189				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-122.2308008	45.28952813	-2.698875565	0.00720641	-211.2242973	-33.2373043
n^5 Na spline	1.060813281	0.044178153	24.01216898	6.72476E-84	0.974003626	1.14762294
n^3 Sr spline	1.384547566	0.108037723	12.81540861	1.75368E-32	1.172254457	1.59684067
(SrNa)	-263268.6863	35088.64825	-7.502958918	3.11728E-13	-332217.6498	-194319.823
Boron	-130.6841103	20.47983589	-6.381111206	4.19602E-10	-170.9267951	-90.4414255
Titanium	33.39124169	5.506716917	6.063729476	2.72302E-09	22.57059477	44.2118886
mg*mod Spline	-1.58999529	0.264890206	-6.002469145	3.87234E-09	-2.110502052	-1.06948853
n^2 Si Spline	-1.815393729	0.359520112	-5.049491444	6.33421E-07	-2.521847365	-1.10894009
Iron	13.33625497	2.896058224	4.604967836	5.30944E-06	7.645527819	19.0269821
$((Fe+0.325)(Mn+0.05))^2$	-40.76106267	9.198145026	-4.431443792	1.16442E-05	-58.83533107	-22.6867943
Manganese	14.88686191	4.218750924	3.528736864	0.000458343	6.597056046	23.1766678
Na Spline $= 1{,}562{,}216{,}460.99*Na^5 - 302{,}724{,}433.82*Na^4 + 21{,}878{,}711.9*Na^3 - 720{,}994.1*Na^2 + 10{,}161.01*Na$						
Sr Spline $= 176{,}630.16*Sr^3 - 30{,}116.56*Sr^2 + 1{,}414.5*Sr$						
Si Spline $= Si^2 - 22.5*Si$						
No TiB function of high significance could be found						

(b) 0.2% Proof Strength

Sodium Modified Samples

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.405142985					
R Square	0.164140838					
Adjusted R Square	0.144333749					
Standard Error	16.82509617					
Observations	217					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	5	11729.54338	2345.908676	8.286974275	3.61024E-07	
Residual	211	59730.69473	283.0838613			
Total	216	71460.23811				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-135.154961	54.65792325	-2.47274234	0.014198419	-242.9005209	-27.4094012
Iron	24.02615771	5.655178601	4.24852324	3.22805E-05	12.87827012	35.1740453
n^2 Si Spline	-1.372956806	0.343189707	-4.000576879	8.74319E-05	-2.049476602	-0.69643701
Sodium	205.0882402	123.0137569	1.667197599	0.096958663	-37.4051683	447.581649
Boron	-30.24424696	57.09906257	-0.529680271	0.596890507	-142.8019531	82.3134592
Magnesium	23.33156636	24.89722422	0.937115164	0.349770697	-25.74760098	72.4107337
Si Spline $=Si^2-25.5*Si$						

Strontium Modified Samples

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.400455791					
R Square	0.160364841					
Adjusted R Square	0.142372659					
Standard Error	15.54488056					
Observations	287					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	6	12922.64316	2153.77386	8.913029061	6.54033E-09	
Residual	280	67660.12728	241.6433117			
Total	286	80582.77044				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-74.70720605	52.31555668	-1.428011299	0.154403018	-177.6890167	28.2746046
Iron	20.19428312	4.779835234	4.224891054	3.23734E-05	10.78530197	29.6032643
n^2 Si Slpine	-0.988011217	0.327721251	-3.014791425	0.002807315	-1.633121963	-0.34290047
Strontium	112.8849378	65.35010958	1.727387123	0.085200867	-15.75505075	241.524926
Boron	-64.32482395	38.05983062	-1.690097483	0.092122256	-139.2446092	10.5949613
Sodium	-1847.741484	1199.996071	-1.539789612	0.124740963	-4209.902492	514.419525
Manganese	6.739340991	4.795617476	1.40531246	0.161036925	-2.700707098	16.1793891
Si Spline $=Si^2-25.5*Si$						

The Full Observation Set

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.385681913					
R Square	0.148750538					
Adjusted R Square	0.137975228					
Standard Error	16.16947208					
Observations	481					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	6	21655.67464	3609.279107	13.80475763	1.7507E-14	
Residual	474	123928.1661	261.4518272			
Total	480	145583.8407				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-95.94592738	39.2348027	-2.445429078	0.014830816	-173.0415886	-18.8502662
n^2 SI Spline	-1.125200614	0.246714754	-4.560734993	6.4985E-06	-1.60999054	-0.64041069
Iron	22.05731326	3.668962835	6.01186609	3.66431E-09	14.84786919	29.2667573
Sodium	277.9990804	99.12473727	2.804537879	0.005245849	83.22080617	472.777355
Boron	-43.27202985	31.36302057	-1.379714997	0.168324901	-104.8997848	18.3557251
Magnesium	25.04727789	15.57570591	1.608099051	0.108479323	-5.55869597	55.6532518
Strontium	35.62357171	56.0218643	0.635886937	0.525157013	-74.45835485	145.705498
Si Spline = Si^2-25.48*Si						

(c) Elongation at Fracture

Sodium Modified Samples

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.856778548					
R Square	0.73406948					
Adjusted R Square	0.722562871					
Standard Error	1.606937328					
Observations	218					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	9	1482.621174	164.735686	63.79546546	5.46604E-55	
Residual	208	537.1074957	2.582247575			
Total	217	2019.72867				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-3.304450604	1.248413746	-2.646919432	0.008744538	-5.765616355	-0.84328485
Magnesium	-31.32564188	2.59531801	-12.07005915	9.0026E-26	-36.44214098	-26.2091428
Iron	-5.873080001	0.638798432	-9.193948678	4.0187E-17	-7.132429178	-4.61373082
n^4 Na Spline	-7493266.502	550759.0749	-13.60534369	1.42328E-30	-8579051.866	-6407481.14
n^2 Si Spline	-0.14341366	0.016170759	-8.868703336	3.39834E-16	-0.175293249	-0.11153407
Titanium	-5.806908226	1.604139331	-3.619952528	0.000370086	-8.969363617	-2.64445283
$((Fe-0.35)*Mn)^3$	396.6224696	120.2931639	3.297132246	0.00114864	159.4723933	633.772546
Manganese	-1.317892209	0.63279601	-2.082649365	0.038505895	-2.565408006	-0.07037641
$B^{0.3}$	-2.305665278	1.159744893	-1.988079699	0.04811423	-4.592026207	-0.01930435
TiB	32.70872553	24.10042648	1.357184511	0.176193446	-14.80368327	80.2211343
Si Spline $= Si^2 - 17.6Si$						
Na Spline $= Na^4 - 0.140974401*Na^3 + 0.00663617*Na^2 - 0.000122504*Na$						

Strontium Modified Samples

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.785255634					
R Square	0.61662641					
Adjusted R Square	0.602786208					
Standard Error	1.422579344					
Observations	288					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	10	901.6390162	90.16390162	44.55328176	5.20174E-52	
Residual	277	560.5737616	2.023731991			
Total	287	1462.212778				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	20.2351311	1.943184872	10.41338443	1.20354E-21	16.40984556	24.0604166
Magnesium	-22.00412332	1.933291582	-11.38168889	7.04061E-25	-25.80993327	-18.1983134
Iron	-3.983766673	0.520001423	-7.661068787	3.10852E-13	-5.007423223	-2.96011012
n^2 Si spline	0.055478336	0.007495048	7.40199903	1.61363E-12	0.040723848	0.07023282
n^3 Sr Spline	16354.80638	2222.256161	7.359550473	2.10625E-12	11980.1509	20729.4619
$B^{0.3}$	-5.170056618	0.709869036	-7.2831133	3.39461E-12	-6.567479888	-3.77263335
TiB	73.73141189	17.89433058	4.120378327	5.00031E-05	38.50526076	108.957563
Manganese	1.29106668	0.495990062	2.603009172	0.009738764	0.314678053	2.26745531
Titanium	-3.02315123	1.366163442	-2.212876686	0.02772153	-5.712532632	-0.33376983
$((Fe-0.35)*Mn)^3$	63.84647864	46.88730171	1.361700851	0.174398772	-28.45421786	156.147175
Sodium	123.8220819	121.8916086	1.015837623	0.310593171	-116.1294606	363.773624
Si Spline $= Si^2 - 34.5539*Si$						
Sr Spline $= Sr^3 - 0.174282*Sr^2 + 0.00898221*Sr$						

Unmodified Sample Set

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.802636926					
R Square	0.644226035					
Adjusted R Square	0.584930374					
Standard Error	0.795273599					
Observations	22					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	3	20.61435462	6.871451539	10.86464043	0.000265259	
Residual	18	11.38428175	0.632460097			
Total	21	31.99863636				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	15.48141753	2.108825438	7.34125132	8.1484E-07	11.05093626	19.9118988
silicon	-1.014049808	0.192064335	-5.279740289	5.08792E-05	-1.417562315	-0.6105373
iron	-2.260569111	0.899704491	-2.512568443	0.021732341	-4.150779568	-0.37035865
titanium	3.137600681	4.054606597	0.773836032	0.449072571	-5.380818276	11.6560196
While titanium has little significance in the above expression it is the thrid						
most significant factor found						

The Full Observation Set

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.860331251					
R Square	0.740169862					
Adjusted R Square	0.734606047					
Standard Error	1.512998139					
Observations	478					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	10	3045.338281	304.5338281	133.0328068	8.3436E-130	
Residual	467	1069.039293	2.289163367			
Total	477	4114.377573				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	4.883680627	0.331942794	14.71241647	1.56834E-40	4.231395028	5.53596623
Magnesium	-26.45239692	1.536296009	-17.21829437	8.40656E-52	-29.47130192	-23.4334919
Iron	-5.034932206	0.405938871	-12.40317832	9.82117E-31	-5.832624111	-4.2372403
n^3 Sr Spline	18800.72225	2498.761716	7.524015648	2.75268E-13	13890.51991	23710.9246
n^4 Na Spline	-7232685.43	435654.0773	-16.60190001	5.51798E-49	-8088769.328	-6376601.53
SrNa	-19469.93905	5704.01813	-3.413372575	0.000697516	-30678.64414	-8261.23397
$B^{0.3}$	-4.062948676	0.617623319	-6.578360229	1.27815E-10	-5.276612005	-2.84928535
TiB	53.56982503	14.44923273	3.707451188	0.000234488	25.17629882	81.9633512
n_2 Si Spline	-0.071788467	0.006135017	-11.70142998	6.49255E-28	-0.083844107	-0.05973283
$((Fe-0.35)*Mn)^3$	194.3730791	40.49081763	4.800423664	2.13498E-06	114.8064257	273.939732
Titanium	-2.730239136	1.03802039	-2.630236518	0.008814348	-4.770005517	-0.69047275
Sr Spline $= Sr^3 - 0.174282 * Sr^2 + 0.00898221 * Sr$						
Na Spline $= Na^4 - 0.140974401 * Na^3 + 0.00663617 * Na^2 - 0.000122504 * Na$						
Si Spline $= Si^2 - 12.75Si$						

Appendix P

Fe/Mn Interaction MLR Anaylsis Outputs

Appendix P Part 1-Varying Iron Range Hv_{10} MLR Outputs

0.1-0.3% Iron Range (ave. Fe= 0.204%)

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.86547968					
R Square	0.74905508					
Adjusted R Square	0.74257311					
Standard Error	1.55889975					
Observations	279					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	7	1965.807649	280.8296641	115.559753	1.42566E-77	
Residual	271	658.5756485	2.430168445			
Total	278	2624.383297				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	33.7126785	1.028077173	32.79197262	2.5205E-96	31.68864551	35.73671151
Magnesium	38.0122626	2.261732979	16.80669776	6.4301E-44	33.55946246	42.46506273
Silicon	1.09594673	0.095131949	11.52028046	2.9333E-25	0.908655149	1.283238321
Manganese	*4.49257684*	*0.53854464*	*8.342069539*	*3.748E-15*	*3.432313903*	*5.55283977*
Titanium	8.72384078	1.169876046	7.457064201	1.199E-12	6.420640421	11.02704115
Strontium	-49.264376	5.90024933	-8.34954137	3.5642E-15	-60.88052651	-37.6482252
Iron	*11.27533*	*2.094562194*	*5.383144043*	*1.5866E-07*	*7.15164833*	*15.3990117*
B^2	-109.68996	41.58071656	-2.63800066	0.00882177	-191.5522388	-27.827677

0.25-0.45% Iron Range (ave. Fe= 0.298%)

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.78730692					
R Square	0.61985218					
Adjusted R Square	0.5912389					
Standard Error	1.3991512					
Observations	101					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	7	296.8573959	42.40819942	21.6630965	4.46306E-17	
Residual	93	182.0590397	1.957624083			
Total	100	478.9164356				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	33.0558737	5.03294552	6.567898184	2.8924E-09	23.0614514	43.05029608
Magnesium	39.7782789	4.879470186	8.152171725	1.6286E-12	30.08862783	49.46792993
Sodium	78.6152934	21.99518307	3.574205003	0.00055926	34.93726265	122.2933241
Manganese	*2.40297675*	*0.905788555*	*2.652911363*	*0.00938425*	*0.604261995*	*4.2016915*
Strontium	-28.338983	8.921626615	-3.17643683	0.00202347	-46.05554795	-10.6224188
Silicon	1.14866367	0.354776454	3.237711122	0.00167072	0.44414865	1.853178693
Iron	*10.770301*	*4.555879942*	*2.364044069*	*0.02015682*	*1.723235355*	*19.8173666*
Titanium	1.80644749	1.601820894	1.12774624	0.26232822	-1.374448165	4.987343145

0.4-0.6^{+}% Iron Range (ave. Fe= 0.623%)

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.86376236					
R Square	0.74608542					
Adjusted R Square	0.73706307					
Standard Error	1.7081381					
Observations	205					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	7	1688.935612	241.276516	82.6930654	3.37701E-55	
Residual	197	574.7939492	2.917735783			
Total	204	2263.729561				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	36.5326607	1.417674969	25.76941931	5.175E-65	33.73689212	39.32842931
Magnesium	35.0119804	2.54201804	13.7733013	1.1343E-30	29.9989172	40.02504358
Silicon	1.05183989	0.103298147	10.18256299	7.8032E-20	0.848127672	1.255552114
Titanium	13.4694412	1.585576381	8.494980991	4.8125E-15	10.34255759	16.59632484
B^2	-384.4906	71.47372042	-5.37946813	2.1062E-07	-525.4425029	-243.5387
Strontium	-37.012046	7.57436839	-4.88648611	2.122E-06	-51.94930712	-22.0747848
Iron	*4.66331505*	*1.913604507*	*2.436927293*	*0.01570087*	*0.889533685*	*8.43709642*
Manganese	*1.22473497*	*0.624462274*	*1.961263346*	*0.05125743*	*-0.006754654*	*2.45622459*

Appendix P Part 2-Varying Manganese Range Hv_{10} MLR Outputs

0.0-0.1% Manganese Range (ave. Mn= 0.006%)

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.87238215					
R Square	0.76105061					
Adjusted R Square	0.75348208					
Standard Error	1.59997453					
Observations	229					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	7	1801.880716	257.4115309	100.55458	4.10457E-65	
Residual	221	565.741991	2.559918511			
Total	228	2367.622707				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	30.7581119	1.209136387	25.43808308	1.368E-67	28.37519812	33.1410256
Magnesium	38.2980619	2.692275108	14.22516659	4.919E-33	32.99224248	43.6038814
Silicon	1.39203368	0.103556268	13.4422929	1.679E-30	1.187949466	1.5961179
Iron	*7.41469242*	*0.648186884*	*11.43912752*	*4.199E-24*	*6.13727372*	*8.69211112*
Strontium	-43.2041	8.485626876	-5.091444674	7.599E-07	-59.9272065	-26.480993
Titanium	8.44845161	1.356179348	6.229597597	2.333E-09	5.775751957	11.1211513
Sodium	30.6211779	13.98614971	2.189392977	0.0296151	3.057878517	58.1844774
B^2	-81.892251	41.22438713	-1.986500148	0.0482132	-163.135492	-0.6490105

0.08-0.35% Manganese Range (ave. Mn= 0.195%)

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.89584237					
R Square	0.80253355					
Adjusted R Square	0.7880406					
Standard Error	1.60503823					
Observations	118					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	8	1141.214134	142.6517668	55.374063	6.33026E-35	
Residual	109	280.800103	2.576147734			
Total	117	1422.014237				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	33.652525	1.871985753	17.97691298	2.191E-34	29.94231228	37.3627377
Magnesium	34.6938011	2.931242426	11.8358689	2.772E-21	28.88417733	40.5034248
Iron	*8.14325896*	*0.687815503*	*11.83930709*	*2.722E-21*	*6.78003181*	*9.50648611*
Silicon	1.0440393	0.126081101	8.28069627	3.404E-13	0.794150809	1.2939278
Titanium	11.9420789	1.96366849	6.081514743	1.797E-08	8.050154087	15.8340037
Strontium	-34.155772	14.78318473	-2.310447462	0.0227458	-63.4555457	-4.8559976
Copper	8.22578836	6.254909332	1.315093141	0.1912385	-4.17123119	20.6228079
Sodium	44.2287024	31.58235624	1.400424404	0.1642265	-18.3664635	106.823868
Manganese	*7.73854779*	*5.24990806*	*1.474034916*	*0.1433545*	*-2.6665931*	*18.1436887*

0.35-0.47% Manganese Range (ave. Mn= 0.447%)

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.83278446					
R Square	0.69352995					
Adjusted R Square	0.60025646					
Standard Error	1.46005159					
Observations	31					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	7	110.9536064	15.85051521	7.4354453	0.000104056	
Residual	23	49.03026453	2.131750632			
Total	30	159.983871				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	49.1990927	9.167388771	5.366750987	1.887E-05	30.23493	68.1632555
Titanium	17.8443839	4.910665274	3.633801714	0.00139	7.685912627	28.0028551
Magnesium	19.0199149	5.91617605	3.214900083	0.0038394	6.781388926	31.2584408
Iron	*3.71799293*	*1.494323091*	*2.48807835*	*0.0205263*	*0.6267543*	*6.80923156*
Silicon	0.75838329	0.223175145	3.398153014	0.0024696	0.296710958	1.22005562
Modification #	-0.2855083	0.208051687	-1.372295118	0.1832078	-0.71589543	0.14487881
Porosity Area	-0.8418783	1.107556631	-0.760122159	0.4549034	-3.13303067	1.449274
Manganese	*-15.461864*	*16.61933212*	*-0.93035414*	*0.3618506*	*-49.8415255*	*18.9177967*

0.35-0.5^{+}% Manganese Range (ave. Mn= 0.501%)

SUMMARY OUTPUT						
Regression Statistics						
Multiple R	0.89148969					
R Square	0.79475387					
Adjusted R Square	0.7831087					
Standard Error	1.5401724					
Observations	150					
ANOVA						
	df	*SS*	*MS*	*F*	*Significance F*	
Regression	8	1295.136261	161.8920327	68.247509	1.05579E-44	
Residual	141	334.470472	2.372131007			
Total	149	1629.606733				
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	37.7613093	2.133918771	17.69575758	1.242E-37	33.54269643	41.9799221
Magnesium	37.8519324	2.755497041	13.73688007	8.667E-28	32.4045014	43.2993633
Silicon	0.84373769	0.106716206	7.906368878	6.931E-13	0.63276698	1.0547084
Iron	*4.18013437*	*0.611249099*	*6.838675717*	*2.236E-10*	*2.97173631*	*5.38853243*
Titanium	10.9885815	1.672899734	6.568583446	9.083E-10	7.68137206	14.2957909
B2	-277.71399	67.61427447	-4.107327804	6.753E-05	-411.382829	-144.04515
Strontium	-23.303265	7.111280639	-3.27694355	0.0013212	-37.3617853	-9.2447452
Porosity Area	-0.9083553	0.401150455	-2.264375614	0.0250765	-1.70140258	-0.115308
Manganese	*4.03302141*	*3.21617521*	*1.253980629*	*0.2119241*	*-2.32513909*	*10.3911819*

Appendix Q
Published Papers

(i) IPENZ94a
"The Effects of Common Melt Treatments Upon the Final Composition and Properties of Aluminium-Silicon Eutectic Castings."

(ii) IPENZ94b
" Quantifying the Physical Effects of Impurities Present in Aluminium-Silicon Castings"

(iii) IPENZ95a
'"The Processing of Molten Aluminium -Silicon Casting Alloys"

(iv) IPENZ95b
"The Physical Effects of Common Impurities Present in Aluminium-Silicon Castings"

(v) IPENZ95c
"The Influence of Melt Contaminants on the Modification and Grain Refinement of Aluminium-Silicon Eutectic Alloys"

Appendix Q-(i) IPENZ94a

The Effects of Common Melt Treatments Upon the Final Composition and Properties of Aluminium-Silicon Eutectic Castings

W.D. Shilvock[1]

Abstract

The melting and casting of aluminium alloys has developed into an exact science over the past 60-70 years. The processing of these alloys in a consistently acceptable manner requires the implementation of several critical and inter-dependent processes. The major processes such as degassing, modification, grain refinement and filtration are discussed, with regard to their effects upon each other and the alloy in question. Although this paper is directed at the processing of the aluminium-silicon eutectic alloy most of the issues discussed relate equally well to the casting of any common aluminium casting alloy.

The results of two sets of experiments are provided. The first illustrate the contamination of molten alloy due to incorrect material selection and handling of foundry tools. The second show the compositional effects various degassing methods have upon the eutectic alloy.

It is concluded that if New Zealand industry is to meet the challenge of being competitive in the modern aluminium foundry environment it must ensure that a complete understanding exists at all stages of production, regarding the processing steps and their effects on the alloy in question.

Introduction

Ninety one and a half percent of the production from NZAS's Tiwai Point smelter is exported, this has made the smelter one of the largest exporters in the New Zealand economy. This fact is not something New Zealand's secondary industry should be overly proud of, as it represents a huge loss of opportunity to add value to one of New Zealand's most important domestic products. Casting represents possibly the single largest area in which local industry may add substantial value to large volumes of NZAS product, yet of the NZAS alloy consumed locally only one fifth is foundry ingot. For local foundries to compete internationally against products from Europe, Asia and the Americas, management and all foundry staff must have an appreciation for the theory and practice associated with modern molten metal processing.

Casting today is more of a science than a black art and involves carrying out a specific set of procedures in a controlled and pre-specified manner. A number of processes take place during the commercial casting of foundry alloy, such as degassing, modification, grain refinement and filtration. Each of these processes has been the topic of extensive research for over fifty years

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and an integral part of commercial practice for almost as long. Even so, they remain the subject of much misunderstanding and scepticism both from foundrypersons and researchers alike.

Although this paper is aimed specifically at the aluminium-silicon eutectic alloy, almost all of the processes and their effects described hereafter apply equally well to most of the other common aluminium casting alloys.

The Aluminium Silicon Casting Alloys

Almost all commercial aluminium foundry alloys contain substantial quantities of silicon. The eutectic alloy is of particular relevance as it has a very low solidification temperature and an extremely narrow temperature band over which solidification takes place; this imparts the alloy with exceptionally good castability. The low solidification temperature as illustrated in the phase diagram (Fig. 1) means casting can take place at a relatively low temperature whilst thin wall and complex shapes can be produced without the incomplete mould filling associated with most other aluminium alloys. The suppressed solidification temperature and presence of large volumes of silicon phase also reduces shrinkage allowing tighter dimensional tolerances, less final machining and less waste in the form of gates and risers. The other major advantages of the eutectic alloy are its exceptional lightness - it is in fact the lightest of the common alloys - and outstanding resistance to corrosion. These factors, as well as moderate strength and ductility without the need for heat treatment, make this alloy useful in a wide range of applications from marine castings weighing several hundred kilograms to household artefacts of a few grams.

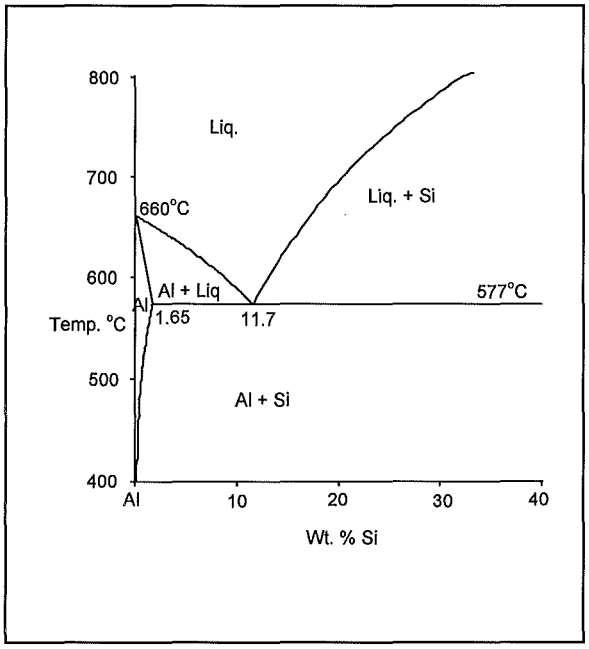


Figure 1:Al-Si Phase Diagram.

Secondary Metal

The most common specification used when ordering eutectic aluminium silicon alloy in New Zealand is British Standard 1490 grade LM6. The LM6 standard is in fact quite wide ranging in its composition specifications and permits from 10 to 13 percent silicon and up to 0.6 and 0.5 percent iron and manganese respectively. This is a specification easily attained by secondary metal producers and so LM6 is available from a number of suppliers with quite substantial levels of impurity including iron, manganese, zinc and copper. This can pose a problem to the founder because secondary alloy usually varies considerably in composition from one batch to another, and these changes in composition within the LM6 range can drastically change the response of the alloy to the treatments performed upon it. Therefore consistency is virtually impossible to achieve unless a sound understanding exists between the metal producer and the founder that very specific limits on composition variation must be maintained.

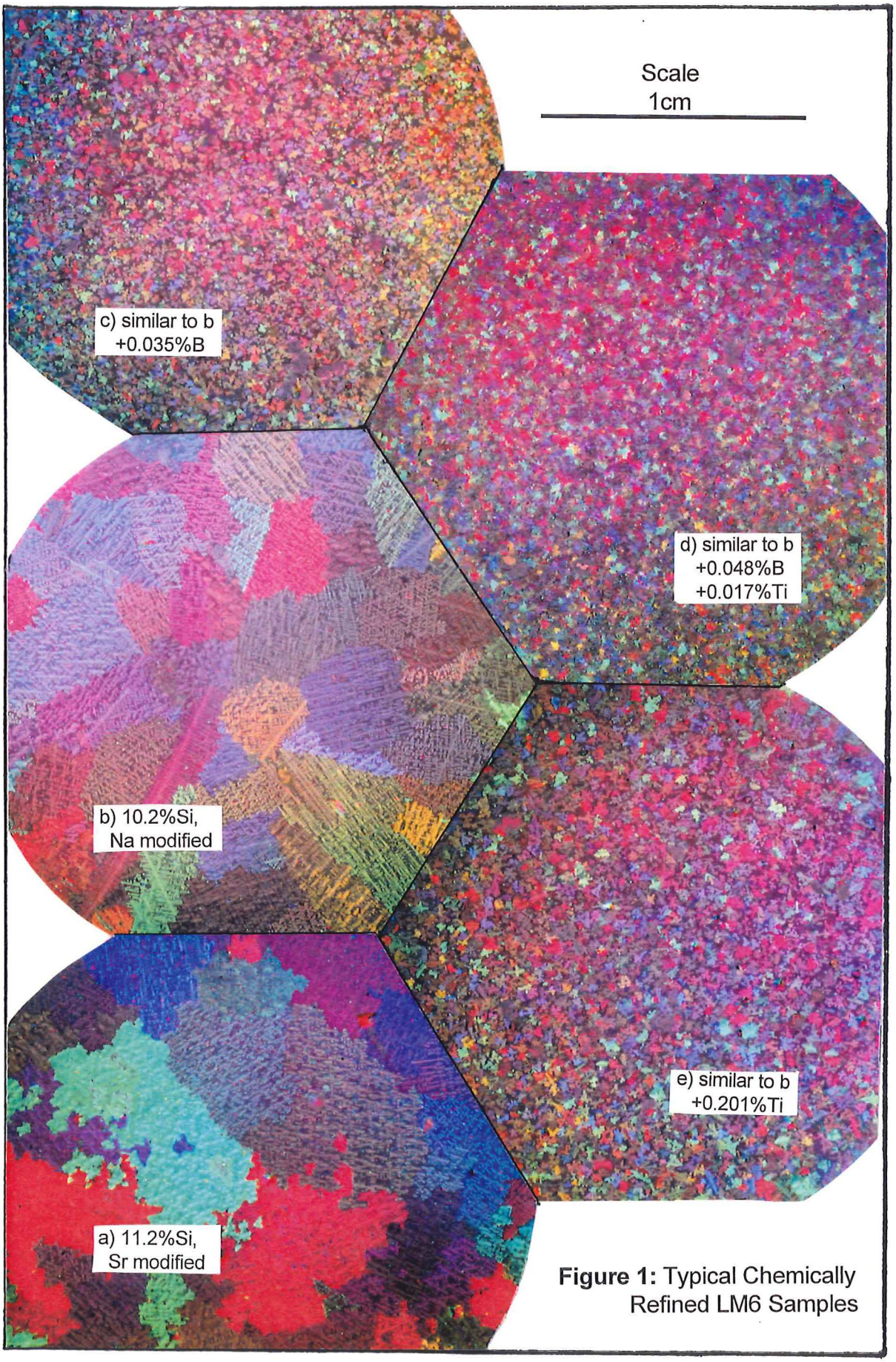


Figure 1: Typical Chemically Refined LM6 Samples

Metal Casting and Processing

Reliably achieving the physical requirements of the LM6 standard necessitates that the base stock composition be controlled, and that the processing of the alloy within the foundry be performed following specific procedures dependent upon the actual alloy being processed. The general metal processing procedure is shown in Fig. 1. Each of the steps shown provides a potential source for contamination, be it from residual cutting fluid, foundry tool erosion or low quality addition alloys. More harm than good can result if any one of these steps is performed incorrectly.

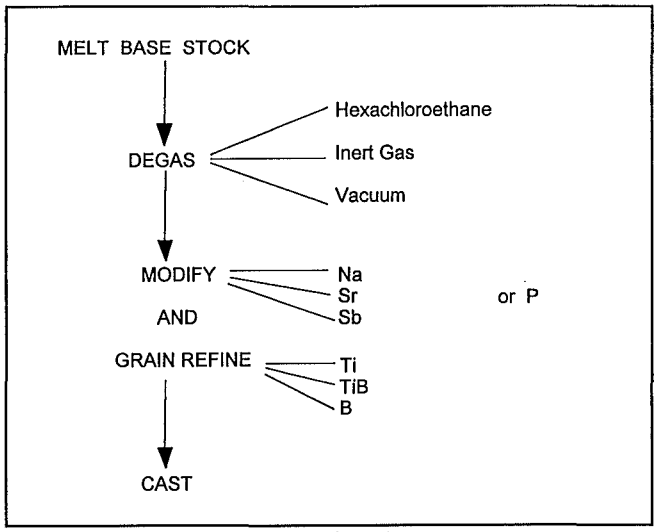


Figure 2: General Casting Route.

Modification

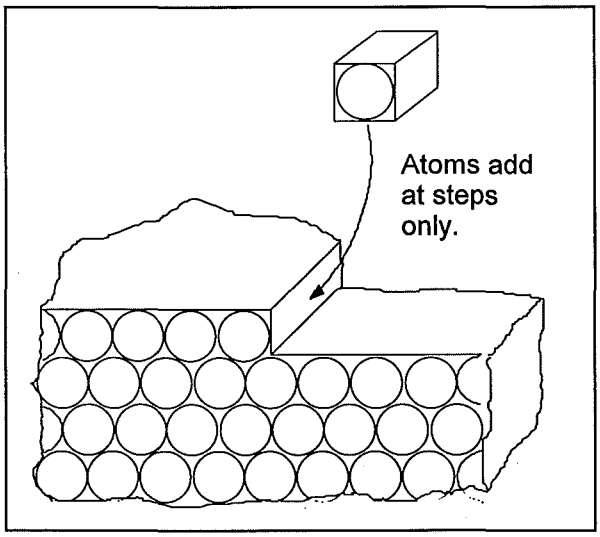


Figure 3: Faceted Solidification of Silicon.

When aluminium-silicon alloys solidify the silicon forms a phase which is very nearly pure silicon; this solidifies in what is know as a faceted manner. As shown in Fig. 3, the dissolved silicon atoms present in the liquid bond on to the solid silicon phase at specific sites such as steps in the crystal surface. This results in the formation of very regular and distinct plates and blocks of silicon. These very large plates have an effect almost analogous to that of graphite in grey cast iron, in that they produce extreme brittleness and limit the ductility causing premature failure before the required strength is attained.

When modifying elements such as sodium, strontium or antimony are added to the melt, even in very small amounts, they cause a progressive refinement of the silicon and change the morphology from plates to inter-connected fibres. This is accompanied by a significant increase in ductility and hence strength. The most powerful of the modifiers is sodium which is required in smaller amounts than either strontium or antimony, and produces a structure finer than that possible with any other modifier. The modifying elements achieve this drastic change in the solidifying silicon's behaviour by bonding to the addition sites and disrupting the crystal structure. This produces very high levels of twinning which in turn allows the silicon to branch out in several directions forming a much finer interconnected network of small plates or fibres.

If excessive amounts of sodium are added then a AlSiNa phase will form which acts as a very strong nucleant of silicon, this causes the formation of moderately coarse silicon particles along the solidifying front. After some growth of this silicon, the liquid is aluminium rich and aluminium is nucleated leaving a very distinct band of coarse silicon, followed by a small band of aluminium. This over-modification is accompanied by a substantial drop in strength although it is preferable to have minor amounts of over-modification than not to modify at all.

Over-modification with strontium is also possible, this results in the formation of Al_4SrSi_2 phase and a coarsening of the silicon. Kanicki[1] reports that "over-modification and its resultant detrimental effects on mechanical properties are a major concern with sodium but not with strontium". Rauta[2] states that "excessive additions of strontium do not cause aluminium banding or silicon coarsening. However undesirable SrSi and $SrAl_2Si_2$ have been observed". It has also been indicated by Kawecki-Billiton[3] that evidence exists to show strontium will reduce the embrittling effect of the FeSi phase, such a phenomena is not reported for the other modifiers.

When strontium is used as the modifier it is usual to purchase pre-modified ingot and for no further modification to take place in the foundry. This is due to the fact that strontium is sufficiently stable within the melt to last through remelting and degassing, *provided reactive gases are not used during degassing.* Sodium on the other hand is relatively unstable in the melt and so must only be added after degassing in the casthouse. Some sodium may well be present in an initial charge due to recycled scrap and reject castings, however as is shown later in Fig. 11, negligible amounts of this will survive degassing irrespective of the method used.

The main states of modification are shown in Figures 4 through 6.

Figure 4: Unmodified LM6, (×50).

Figure 5: Modified LM6, (×100).

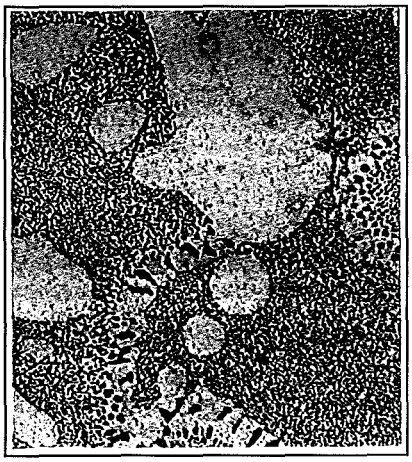


Figure 6: Overmodified LM6, (×100).

It should be noted that refinement of the silicon phase is possible by increasing the cooling rate, and if permanent metal moulds are used it is often possible to achieve quite acceptable physical properties without the need for complete or even partial modification. The increased chilling rate does not change the shape or nature of the silicon, only its size, so modification can still result in further substantial improvements in the physical properties of the cast alloy.

Degassing

As shown in Fig. 7 the solubility of hydrogen in aluminium increases rapidly with temperature. Upon cooling and solidification this dissolved hydrogen will come out of solution in the form of bubbles resulting in porosity. Natural degassing by holding the melt at low temperature prior to casting is too slow to be of commercial significance. Hydrogen pick up by the melt is unavoidable but can be reduced by minimising any moisture or hydrocarbon sources present, particularly those associated with incompletely cleaned and dried, base metal, tools or crucibles.

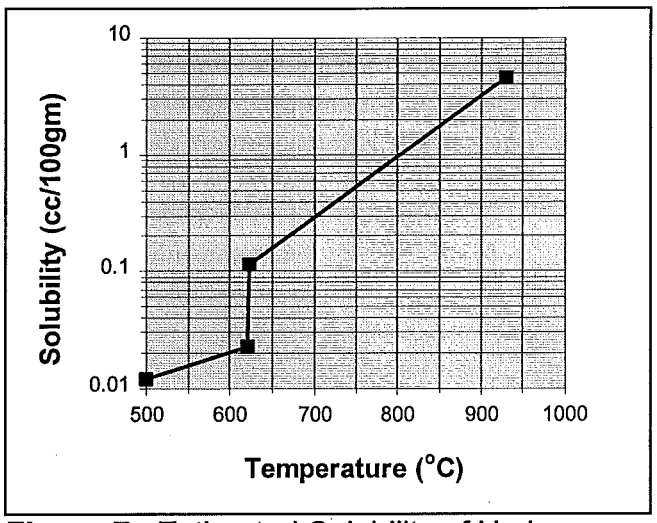


Figure 7: Estimated Solubility of Hydrogen in LM6.

There are several degassing methods which facilitate the removal of hydrogen from the melt prior to casting. All of these methods use one of three basic mechanisms. The least common of these is vacuum degassing which involves drawing off the hydrogen by exposing the melt surface to a reasonably high vacuum. This method is in commercial use in some of the larger foundries in Europe and the United States but is not used by smaller foundries as found in New Zealand.

The second mechanism involves introducing a reactive gas such as chlorine or fluorine to the melt. Bubbles of these gases react with the atomic hydrogen present and rapidly strip the melt of excessive gas. The reactive gases are usually introduced via decomposing tablets such as hexachloroethane or by direct injection. When direct injection is used the reactive gas is usually mixed with argon or nitrogen. Direct injection of the gases can be achieved using ports within the furnace base, lances or submerged rotary impellers. Degassing efficiency increases with a decrease in bubble size and one of the most efficient methods of achieving a fine dispersion of bubbles is to use a submerged porous impeller.

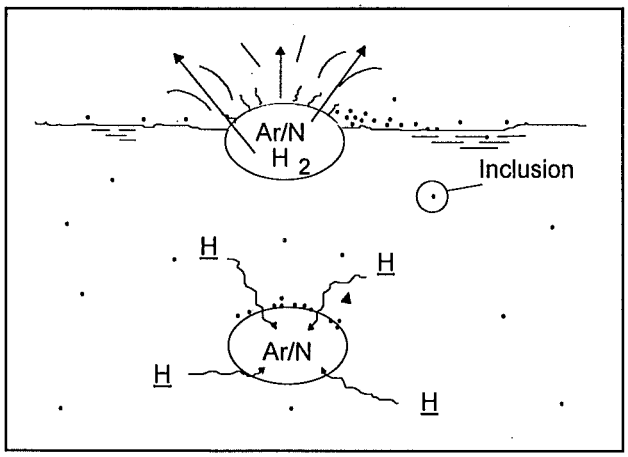
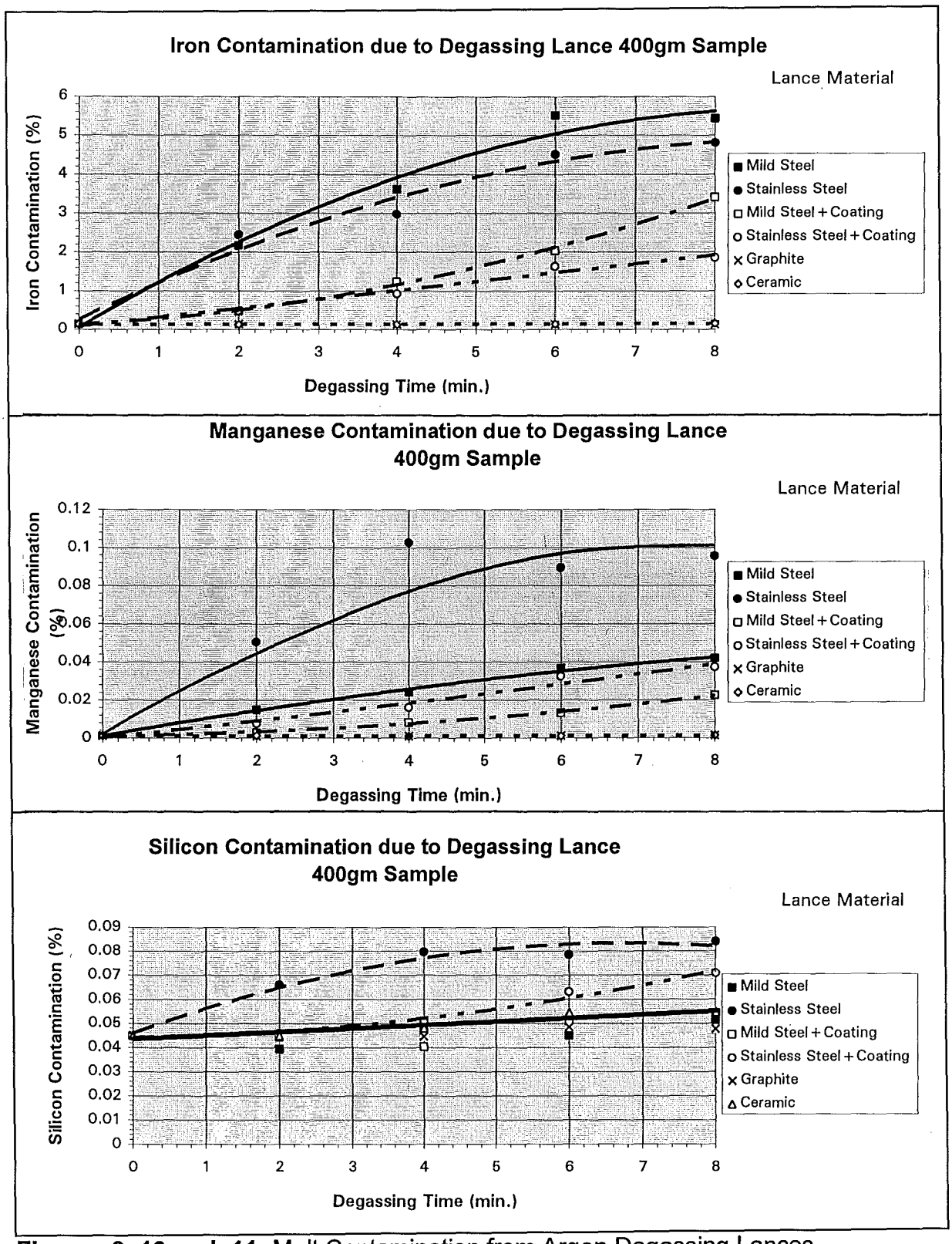


Figure 8: Inert Gas Degassing.

An increasingly popular method of degassing is to introduce an inert gas such as argon or nitrogen. As shown in Figure 8, bubbles of these gases provide a medium into which the atomic hydrogen will diffuse. The bubbles then float to the surface to release the hydrogen into the atmosphere. Figure 8 also illustrates how the bubbles of gas help flush any suspended oxides and undissolved media to the surface so that it may be integrated into the surface dross.

Degassing Lance Requirements

Figures 9 through 11 illustrate the results of a set of experiments designed to highlight the contamination of a melt by the degradation of degassing lances. The results also highlight the effectiveness of alumina type coatings such as Abel-Lemons "Alcoat D" in protecting exposed materials in contact with the molten aluminium.



Figures 9, 10 and 11: Melt Contamination from Argon Degassing Lances.

These experiments were performed by exposing small quantities of high purity aluminium (400g) to large argon lances (approx 12mm O.D.) at a constant temperature of 780°C. Consequently these results overstate the level of contamination which could be expected commercially, however they do provide a clear indication as to the suitability of the various lance materials used.

It should be noted that although the alumina coating proved its worth by reducing contamination by 50-60 percent the only really acceptable materials used were the ceramic (in this case a mullite type) and graphite. The current high costs associated with ceramics capable of reliably withstanding 700-800°C thermal shock loadings, restricts their use mainly to areas other than commercial foundry tools.

These results highlight how much caution must be exercised when exposing conventional materials to highly reactive molten aluminium.

Impurity Removal by Degassing

It has long been known that degassing will aid the removal of inclusions as well as some alloy elements, the modifiers being particularly sensitive in this regard. A set of experiments has consequently been carried out to investigate which elements are removed and their rates of depletion. The experiments involved melting a 4kg charge of eutectic alloy and then monitoring the metal composition as degassing took place. The alloy was initially boosted to the maximum permissible levels of magnesium, manganese, zinc and iron. The grain refiners titanium and boron and either sodium or strontium modifier were also added in amounts typical of those found commercially.

The degassing methods used were lance injection of either argon or nitrogen, or tablet additions of chlorine or nitrogen. Experience with similar size melts and lance injectors has shown comprehensive degassing to take less than five minutes. The nitrogen degassing tablets (Foseco Degasser 610) are specifically designed to be used with strontium premodified ingots so as to minimise modifier removal and eliminate the need for inert gas hydrogen purging equipment. Hence these tablets were only used when strontium was used as the modifier.

It should be noted that the chlorine tablets used (Foseco Degasser 190) are also sold as grain refiners hence it was surmised that they would not cause the removal of titanium or boron at the same rate as the other processes investigated.

The level of variation in composition for the major impurity elements affected are illustrated in Figures 12 through 21.

Points to be observed are:-

- The very rapid removal of sodium was independent of the type of degasser used. This can be directly compared with the very gradual extraction of strontium.

- The formation of NaCl is thermodynamically far more favourable than $MgCl_2$, consequently sodium should be removed before magnesium as indicated by Neff[4].

However figures 20 and 21 show that magnesium is removed far faster in the presence of either sodium or a reactive gas. This supports the practice of not using sodium salt cover fluxes on alloys containing magnesium if the level of magnesium present is to be retained.

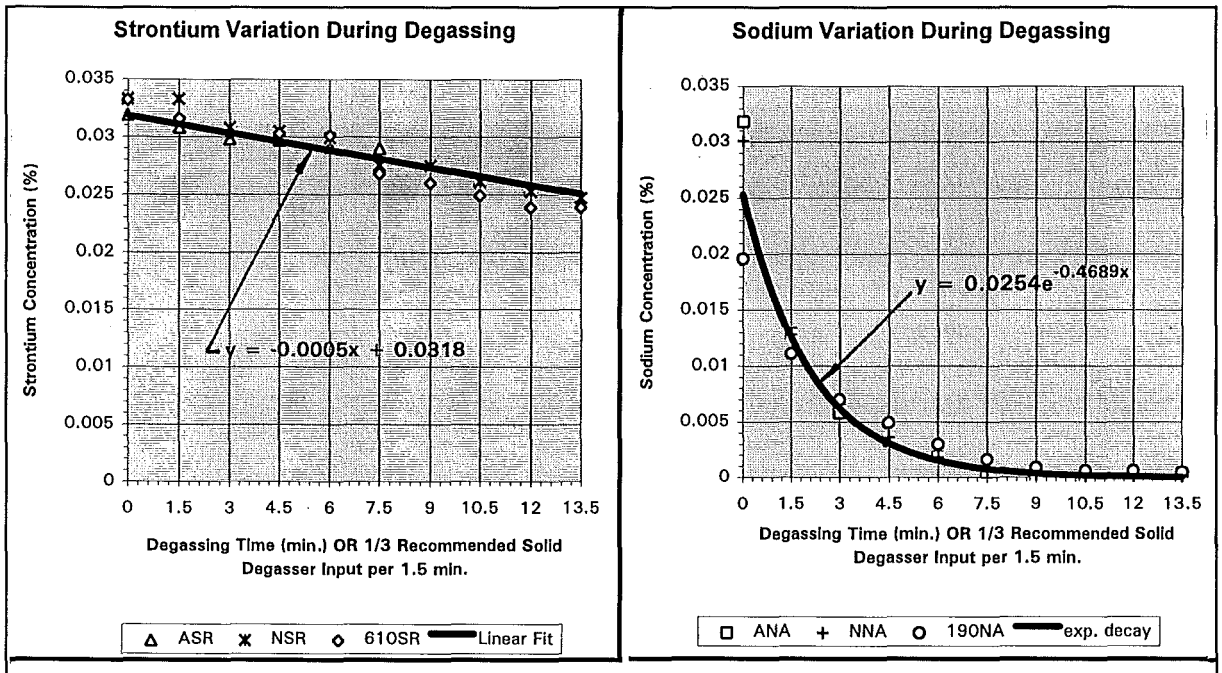
- Silicon is removed faster in the presence of sodium. This may be due to the formation of $(NaAl)Si_2$ and the silicon being extracted with the sodium rather than the precipitate breaking down.

- Silicon does not appear to be removed faster in the presence of magnesium, even though the magnesium is likely to be present as Mg_2Si or $FeMg_3Si_6Al_8$.

- Both the titanium and boron concentrations fell significantly irrespective of the degassing method used except ....

- The degasser 190, which is promoted as a grain refiner and degasser did appear to promote the retention of boron levels, but had little if any effect on the level of titanium remaining in the melt.

It must be concluded from this work that degassing methods should not only be selected dependent upon the initial alloy composition but the degassing times and amount of returned feed stock must be closely monitored, otherwise maintaining product composition and hence physical consistency becomes virtually impossible.



Note: A 10 minute reheat of these casts took place after 6 minutes degassing.

A_ _ = Argon degassed. _NA = Sodium added as initial modifier.

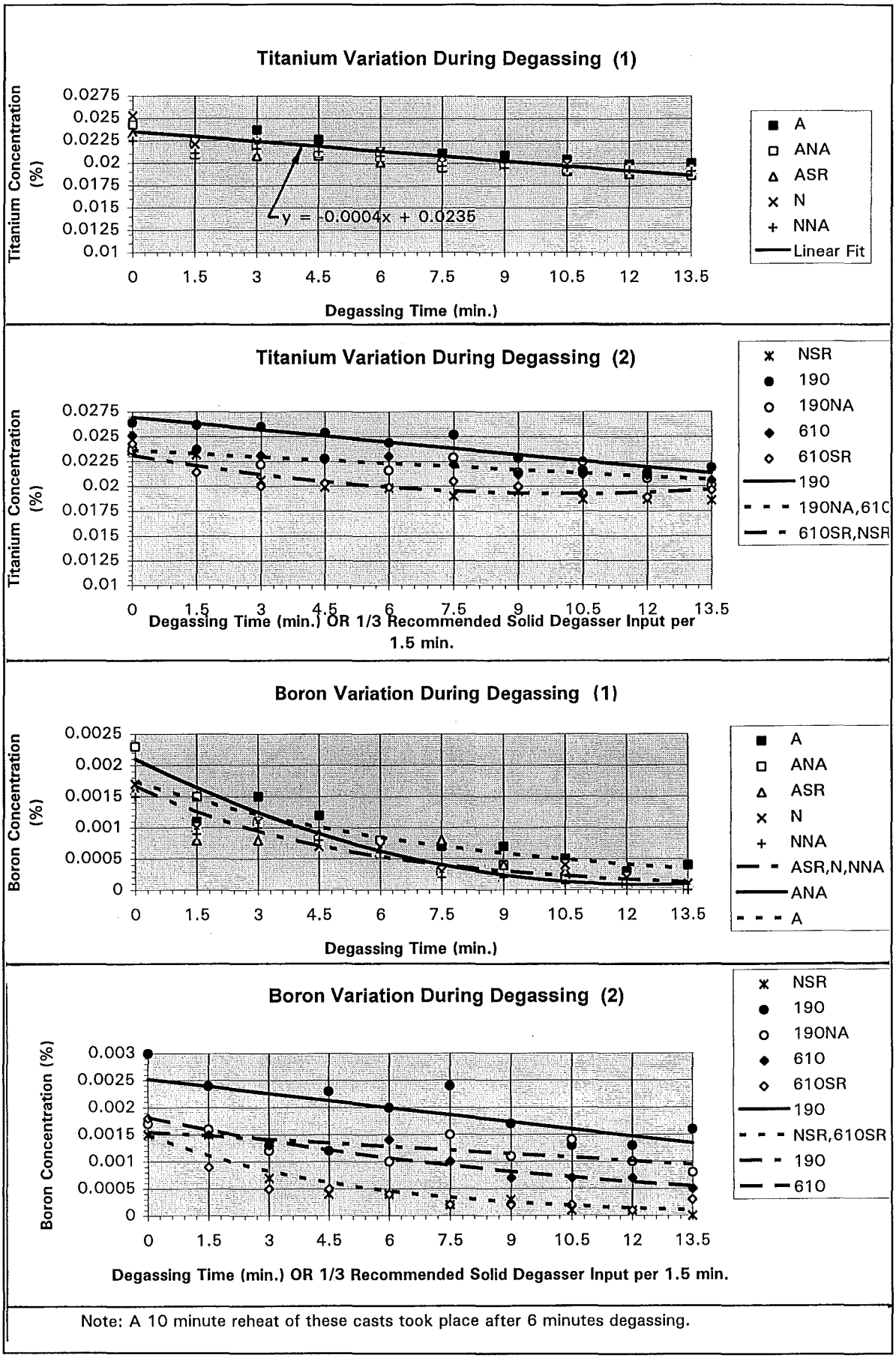
N_ _ = Nitrogen degassed. _SR = Strontium added as initial modifier.

190_ _ = Foseco "Degasser190" degassed - This product uses Chlorine as the purging gas and also acts as a grain refiner.

610_ _ = Foseco "Degasser 610" degassed -This product uses Nitrogen as the purging gas and is designed specifically for use with Strontium premodified ingot.

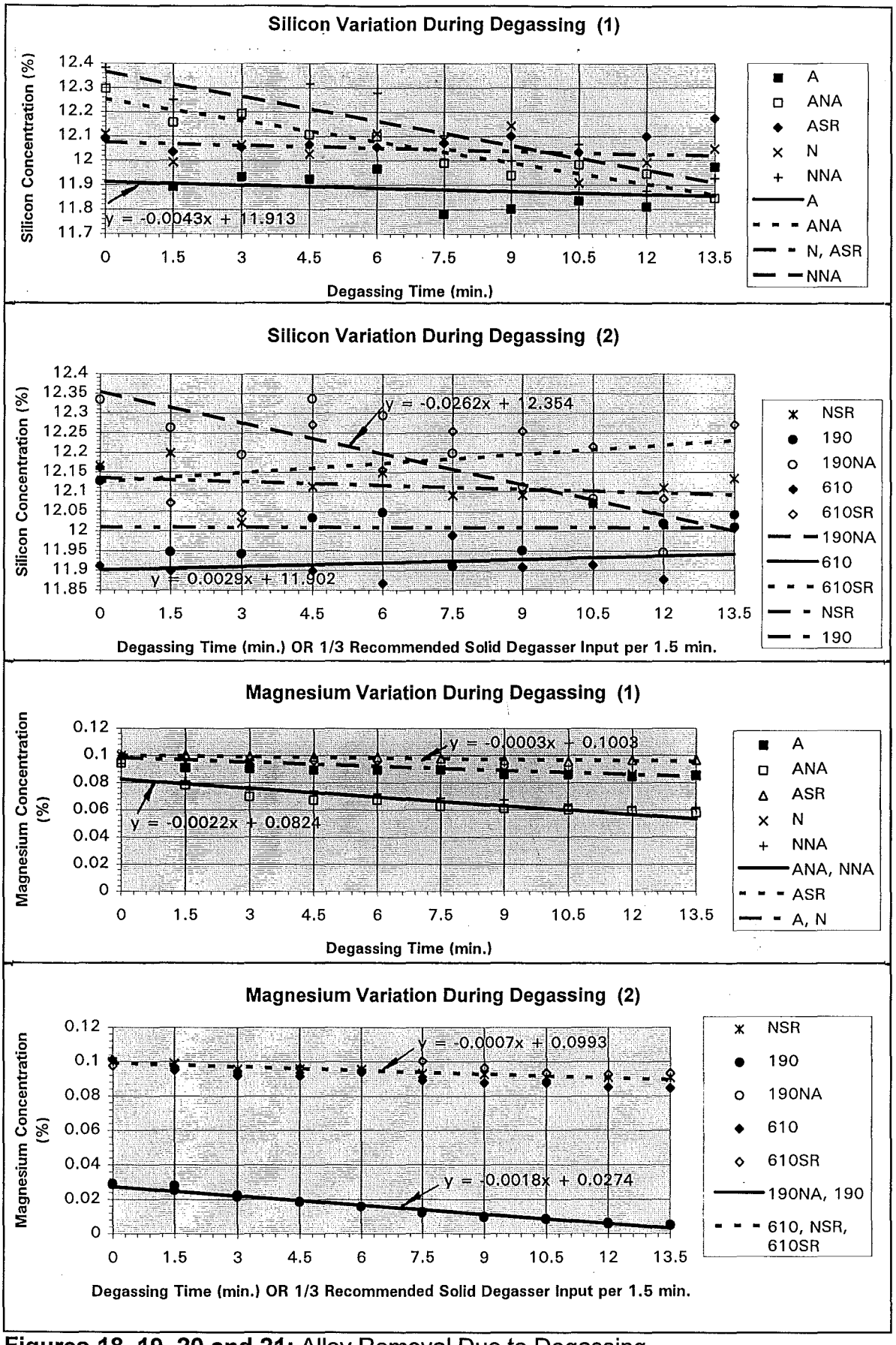
Gas flow rate used = 2.4l /min. (0.142m^3/Hr.).

Figures 12 and 13: Modifier Removal Due to Degassing



Note: A 10 minute reheat of these casts took place after 6 minutes degassing.

Figures 14, 15, 16 and 17: Grain Refiner Removal Due to Degassing.



Figures 18, 19, 20 and 21: Alloy Removal Due to Degassing.

Grain Refinement

Al-Ti and Al-Ti-B grain refiners have been in widespread commercial use for many years. Despite countless investigations the mechanisms behind the refining processes are still poorly understood and scepticism surrounds the practical worth of this treatment. The ability of certain elements to achieve grain refinement is beyond question, however any mechanical advantages resulting from the grain-refinement of high silicon alloys are reported to be minimal to non-existent. Vass[5] states "the mechanical properties obtained do not appear to be significantly effected by the titanium level, the amount of the addition or the grain size", an opinion which is shared by Sigworth[6]. There is agreement that a fine grain size reduces the size of porosity present, resulting in a fine dispersion of voids rather than a few large pores. This is reported to have little effect on the mechanical properties other than to improve the consistency of results; in other words better mechanical properties can not be expected but less variation between melts and within castings should be encountered. It is also generally accepted that the grain-refined metals' ability to disperse porosity greatly assists casting soundness, particularly with large castings.

Figure 22 (from[7])illustrates the effects of various grain refining master alloys on commercial purity metal. It can be seen that fade is quite a problem when pure titanium is added(a) but additions of boron(b and c) greatly increase the period over which refinement lasts. It must be stressed that the response of a master alloy is extremely dependent upon its thermal history, not just its composition. Titanium dissipates into the melt as $TiAl_3$ which is an extremely effective nucleant of aluminium requiring very little undercooling. It is normal practice to add around

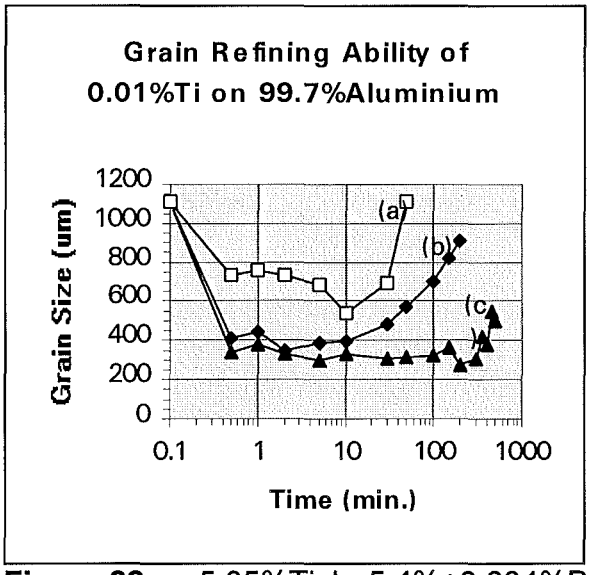


Figure 22: a=5.35%Ti, b=5.4%+0.034%B c=5.0%Ti+0.2%B.

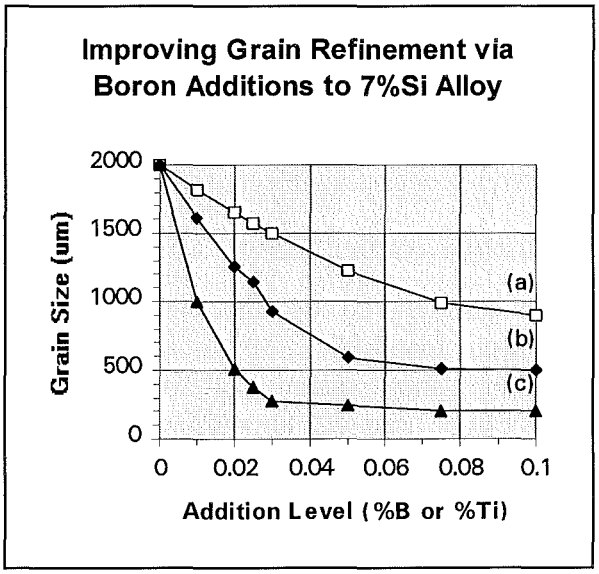


Figure 23: a=Al+5.0%Ti, b=Al+5.0%Ti+1.0%B,c=Al+4.0%B.

0.01 - 0.02% titanium, however a peritectic reaction occurs at 0.15% titanium causing the $TiAl_3$ to dissolve, the result being that titanium refinement is subject to fade as shown above. Numerous theories regarding how boron reduces this fade have been proposed but Guzowski, Sigworth and Sentner [8] propose what is possibly the most complete explanation. They noted that grain refinement is most effective when borides are attached directly to the titanium

particles. From this they proposed that the titanium rich regions surrounding the titanium sites, even following the titanium's solution, promote undercooling to the point where AlB_2 can act as a nucleant. This necessity for undercooling makes boron alone totally ineffective in the refinement of purer alloys. However this is not the case with alloys displaying suppressed solidification temperatures as is the case with the eutectic alloys and others containing appreciable amounts of solute. Although it is not commercial practice to use boron alone, boron has been shown[7] to promote a finer grain size than the titanium or titanium-boron mixes. This can be seen in Figure 23 (from[8]). An illustration of the degree of grain refinement gained with the eutectic alloy is shown in Figure 24.

Filtration

Filtration to remove oxide and other insoluble contaminants within the melt has become an integral step in the production of high quality castings. These contaminants not only directly reduce strength, ductility and fatigue resistance but also entrap substantial pockets of gas. It is stated by Clegg[9] that the oxide also acts as a reservoir for hydrogen even after comprehensive degassing, hence their association with unwanted porosity.

Modern filters are generally made from alumina and may be used at any step in the metal transfer process, but the most common and effective position is in the mould feeder. In the mould they not only filter but cut down turbulence during mould filling and this in itself reduces oxide entrapment as well as mould erosion. One of the major achievements of the in-mould filter is to remove large titanium and boride particles which may have been introduced via excessive or low quality grain refiners. The coarse grain refiner particles along with any carbides present greatly reduce melt fluidity and produce "hard spots" within the casting. The nett effect of these, and the oxides upon secondary manufacturing operations is to greatly reduce cutter life and increase scoring due to swarf pickup.

Effective filtration when carried out by ceramic filters embedded in the mould feeders has been reported to cut casting rejections by as much as 90%[10].

Cover and Cleaning Fluxes

Fluxes based on the NaOCl-KCl system are widely used as covers and cleaning agents in most aluminium foundries. The NaOCl - KCl salts melt and form a molten layer on top of the aluminium, thus protecting it from both oxidation and reaction with moisture. While most fluxes can be used with almost any alloy those containing sodium salts are not recommended for high magnesium alloys. The reason for this is that magnesium tends to be displaced by sodium resulting in significant losses of magnesium to the dross. When magnesium alloys are used it is usual to apply a flux based on the $MgCl_2$ - KCl system.

The cleaning action associated with most cover fluxes comes about by the addition of sodium flurosilicate ($Na_2Si\ F_6$). The flurosilicate effectively coats the aluminium oxide layer allowing turbulence to mechanically strip away the oxide from its aluminium core the oxide will then float to the surface and be removed with the dross. The traditional method for adding fluxes is to manually apply salts to the melt surface, then to rabble them in so that they may react with any oxides present. The alternative method is to use flux injection and blow flux into the melt through an inert gas lance. This combines degassing and fluxing into one step and allows the flux to react throughout the entire melt rather than just within the surface region.

Conclusions

The main conclusions to be drawn regarding the casting of aluminium alloys and in particular the eutectic alloy are:

- If the required physical standards of BS1490 LM6 are to be consistently surpassed by a reasonable margin then foundry management and staff require a complete understanding of the mechanisms and full effects of all of the processing steps which take place.
- Implementation of stringent base metal and additive standards regarding initial composition and subsequent handling are just as vital as consistency in the processing steps themselves.
- Contamination from sources such as the surface oxide layer and foundry equipment must be reduced as much as practicable.

Finally, the choice of processing route and additives to be used must be made knowing the exact characteristics of the alloy in question and the application (eg mould size and type) for which it is being used.

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Quantifying the Physical Effects of Impurities Present in Aluminium-Silicon Castings

W.D. Shilvock[1]

Abstract

The Aluminium-Silicon eutectic alloy has been in use for over 70 years, yet the quantitative effects most common melt treatments have upon the resulting mechanical properties remain largely unknown. Interrelationships between the bulk of the impurities commonly found in aluminium-silicon castings and the mechanical and physical properties also remain unquantified. This paper outlines a set of experiments performed at The University of Canterbury to resolve these issues.

The casting and analysis of 495 aluminium-silicon test bars within the composition range of British Standard LM6 has been performed. The composition variables included silicon, iron, manganese, magnesium, sodium, strontium, titanium, and boron. These castings were monitored for; tensile strength, ductility, grain size, hardness, modification level and porosity. The accumulated data from these experiments has been tabulated, and the preliminary results of multi-linear-regression analyses are presented. Also included are microstructures showing the phases associated with most of the above mentioned impurities.

Notable indications from the results to date include:(i) the commonly reported detrimental effects of iron on ductility seem insignificant, while it's ability to increase the proof strength is marked;(ii) sodium modification provides significant strength advantages over the use of strontium;(iii) strontium causes ductility to decrease when present in levels beyond 300ppm, however this drop in ductility is not accompanied by lower strength;(iv) when increasingly excessive amounts of sodium are added strength recovers slightly, and finally,(v) while titanium additions are reported to improve casting soundness and have little effect on strength, analyses performed to date have shown the gains in strength attributable to titanium addition to be significant.

Introduction

The aluminium-silicon eutectic alloy has been one of the most important aluminium foundry alloys in use since 1920 when Pacz discovered that the solidifying silicon phase could be refined by a process known as modification. Since that time several other procedures have been adopted as integral steps in the casting of this alloy, such as; degassing, filtration and grain refinement, as discussed in the preceding paper. Countless investigations have been carried out

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into each one of these processes, however one thing that comes to light very quickly is that these investigations have almost always been performed from a metallurgical perspective. That is they have set out to establish why and how the processes work as opposed to quantifying the physical significance of variation within each melt treatment.

Very clear standards exist regarding how to quantify the various states of modification. The point at which modification ceases to be physically advantageous, and over-modification with its associated detrimental effects begins is also well established. Even so no clear guidelines exist quantifying the change in mechanical properties that can be expected due to variation in the level of modification. There is also very little information, quantitative or otherwise, regarding the effects impurity elements have on modification, grain refinement or porosity, with the obvious exception of the modifying and grain refining elements. Gruzleski[1A] makes note of this point and draws attention to the fact that most of the published information to date has been contradictory.

An example of the variation in grain size possible, without the addition of grain refiners, is shown as A and B in Figure 1. The samples illustrated were cast from the same temperature and experienced similar cooling rates. They are of very similar composition and vary only by the alloy concentrations indicated.

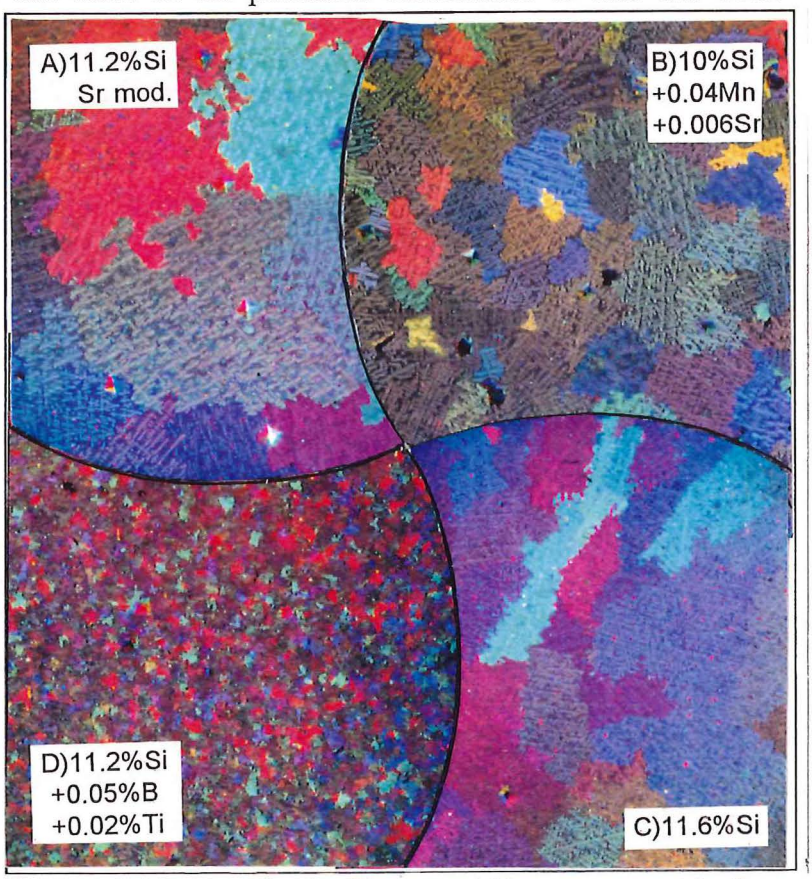

Figure 1: Various Grain Sizes and Types present in the Cast Test Bars, (×4.4).

It should be noted that BS1490-LM6 is the most common specification used in New Zealand when referring to the Aluminium-Silicon eutectic casting alloy. Other commonly used designations include Australian Standard 1874-401 and ISO 3522 Al-Si12.

Controversy surrounds several common practices associated with the aluminium-silicon alloys, such as the addition of manganese to reduce the embrittling effects of iron. This practice relies on the removal of $FeSiAl_5$ needles present within the eutectic by the formation of $(FeMn)_3Si_2Al_{15}$ which usually appears in the shape of Chinese script within the primary aluminium dendrites. It is well established that these structures do form, however their effects on the mechanical properties is still open to debate, particularly with reference to the sand cast eutectic alloy. Detailed investigations[2] on Al-Si-Mg casting alloys have shown that the embrittling effect is more pronounced in chill castings than sand castings, and that it shows up far more clearly in impact tests than by conventional tensile testing. It is also widely

reported[3][4] that excessive levels of iron are directly detrimental to ductility, something that previous studies at The University of Canterbury[5] have failed to substantiate.
Research is currently under way at The University of Canterbury to resolve these issues, and to provide quantitative results showing the interrelationships between the mechanical and physical properties and chemical composition. This will provide previously unavailable information for anyone processing the eutectic aluminium-silicon alloy, and will improve the chances of foundries reliably achieving the stringent physical requirements of B.S. 1490-LM6.

Experimental Procedure

The impurities and their composition ranges to be investigated were selected so as to be as wide ranging as possible within the LM6 standard. The elements singled out for investigation were chosen because they are routinely found in eutectic alloy processed locally, particularly when secondary base metal is used. Zinc was not included in the investigation as it is well reported[4] that its influence on room temperature properties is minimal when present in concentrations as high as ten times that permitted by the LM6 standard. The final composition variables used are shown below along with the ranges in which they were cast.

Silicon	10-11.5-13%
Iron	0-0.6%
Manganese	0-0.2-0.5%
Magnesium	0-0.1%
Sodium	0-(0.015)-0.05%
Strontium	0-(0.025)-0.05%
Titanium	0-0.2%
Boron	0-0.05%

The values in brackets represent the typical modifier additions made.

Specific concentrations of each element were aimed for, these values usually being the limits listed above. However experimental scatter resulted in a range of compositions being produced covering the entire composition spectrum.

Casting Procedure

Where possible all processes and equipment used during casting were designed to model commercial foundry practice. All casting was carried out utilising a gas fired furnace, conventional clay/graphite crucibles and low carbon steel foundry tools. All tools and crucibles were coated in Abel-Lemon "Alcoat D", an alumina based refractory, to reduce melt contamination and prolong tool life. At the completion of casting some material loss from the tools was evident, however the amount was minimal considering that 270 melts had been made.

Melt sizes varied from 1.1kg if a single specimen was cast, to 4kg when four specimens were to be produced. All test bars were cast using identical sand moulds supplied by C.W.F. Hamilton Ltd and complying to B.S. 1490. At the same time composition disks were cast for later spark emission analysis at New Zealand Aluminium Smelters Ltd, the analysis providing composition results for 21 elements including all of those mentioned above. The base material used during casting was NZAS CA401F, an aluminium-silicon eutectic alloy routinely supplied to the domestic market. This alloy was supplied unmodified with minimal impurity other than an iron level of 0.18%. Where necessary the silicon levels were reduced by the addition of

commercially pure aluminium, while the levels of most other elements were adjusted by the addition of commercial master alloys, the exceptions being magnesium and sodium which were added directly as pure metal. The addition of boron was carried out using two master alloys one containing 5% titanium 1% boron and the second being 3% boron. Particular care was taken when ordering the 3% boron master alloy to ensure the alloy contained predominantly AlB_2 and not AlB_{12}, as the more common AlB_{12} is not an effective grain refiner.

As is normal practice melts were not allowed to exceed 800°C and modification took place in the range 720-740°C following degassing. All final pouring was carried out in the temperature range 700-720°C

Degassing

Degassing was performed by injecting pure argon into the melt via a graphite lance. Low pressure tests (Straube-Pfeiffer tests) revealed that comprehensive degassing of the base material (CA401F) had taken place after five minutes. This degassing time was subsequently used for all melts irrespective of the amount of porosity being observed in the final castings. This was done so that any increased porosity, due to shrinkage or gassing, could be related back to the impurity additions made.

When inert gas degassing is performed commercially nitrogen is used as the gas medium, however for these experiments argon was used. The reasons for using argon were, the availability of certified high purity gas to minimise contamination when supply pressures fell and the availability of alternate gas supplies should they be required during melting. The similarity in the way argon and nitrogen perform was demonstrated in the degassing experiments detailed in the previous paper. As a result it was considered unlikely that the use of argon instead of nitrogen would have affected the degassing process.

Fluxing

Early melts had fluxing covers applied in the form of Foseco "Coveral 11". However, this process was stopped due to contamination of test bars by particles of cover and dross. This was brought about by a build up of flux forming on the crucible wall which was extremely difficult to extract and tended to be dislodged during pouring. It is unlikely that this problem would be encountered when melting larger volumes of metal, as the crucible would be far easier to clean and the amount of flux added per kilogram of metal melted would be substantially lower.

Physical Testing

Tensile Testing

All cast tensile test specimens were machined and then tested in accordance with B.S.18. The samples had a diameter of 11.28mm and were tested on a computerised Satec Universal Testing Machine. This provided tensile strengths, 0.2% proof strengths, elongations to failure and stress strain curves. Examples typical of the stress strain curves obtained are shown in Figure 2.

Hardness Testing

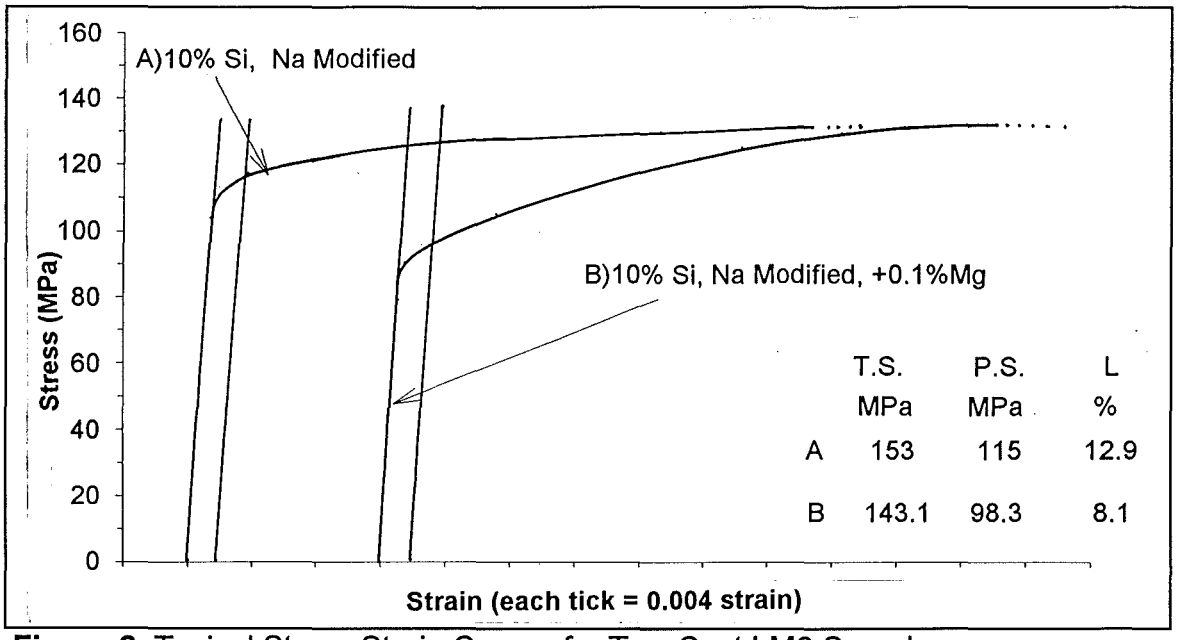

Figure 2: Typical Stress Strain Curves for Two Cast LM6 Samples.

Samples were also hardness tested using Hv_{10} in accordance with B.S.427. To compensate for variation in hardness across the test piece diameter six hardness tests were performed in a traverse across each sample, and then averaged. This revealed that some samples were substantially harder in their core than their edges, while others showed the opposite trend. While no statistical analysis has yet been performed to investigate these trends, no obvious correlations seem to exist between composition, modification and these hardness traverse irregularities.

Modification Level

The modification rating for each sample was established using standard AFS(American Foundrymen's Society) modification scales[6], and then multiplying each scale value by the proportion of the sample area which it represented[1B]. For example if 20% of a samples area is rated 2, 65% rated 3 and 15% rated 4, then the modification rating is...

$$(0.2\times2)+(0.65\times3)+(0.15\times4)=\underline{2.95}$$

Grain Size

It was initially hoped to produce an image of each sample which would allow the grain size to be accurately measured by a computerised image analyzer. Unfortunately the only method found for creating suitable images involved manually tracing the grain boundaries from photographs such as those shown in Figure 1, this was regarded as too slow to be used on all 495 samples.

Revealing the grain structure of aluminium alloys containing less impurity than is normally found in casting alloys is best achieved using cross-polarised light on polished, etched and anodised surfaces. This does not reveal the grain boundaries but does highlight each grain in a different colour. This method was attempted with the LM6 samples using several different

etchants and anodising conditions however only limited success was achieved. The eventual method used to clearly reveal the grain structure of the specimens involved projecting light of varying colour onto the macroetched samples from different angles. This was the method used to produce the images shown in the preceding paper and Figure 1. These colour images are of known magnification, and this allows the grain size to be assessed via comparison with ASTM Standard E122 grain size plates[7]. This method for quantifying grain size is designed for structures displaying equiaxed grains only. As a result the 5 to 10 cast samples displaying large columnar regions, as shown by C in Figure 1, required analysis using traced grain boundaries and computerised image analysis.

Porosity

Sample porosity has been quantified visually using a set of six standard samples ranging from 0 to 1.07% porosity by area. The standard sample porosity areas were established using image analysis, a method which was not used for all of the samples as it was extremely time consuming and involved creating further photographic images of each sample.

Porosity levels could have been quantified by density measurements, however due to the large volumes of impurity present the theoretical density of each specimen would have had to be calculated. This would have been time consuming and would have introduced errors associated with composition analysis as well as any error present in tabulated density charts.

The Effects of Phosphorus

Phosphorus acts as an extremely strong nucleant for silicon phase solidification. This promotes coarsening of the silicon structure so opposing the refining action of the modifiers. This is sometimes regarded as beneficial in hypereutectic alloys where phosphorus is often added to achieve a fine and even dispersion of primary silicon, improving ductility and wear resistance. In the hypoeutectic alloys where refinement of the eutectic silicon is desired phosphorus contamination should be minimised where ever possible. Phosphorus usually enters the aluminium from contact with refractories, tools and crucible glazes, and is often present in virgin alloy at around 4-5ppm and at ever higher levels following subsequent processing. Its effect on modification has is shown in Figures 3 and 4[1C][8]. From these figures an increase in phosphorus level from 5 to 8ppm can be seen to more than double the amount of modifier required to achieve a similar level of modification.

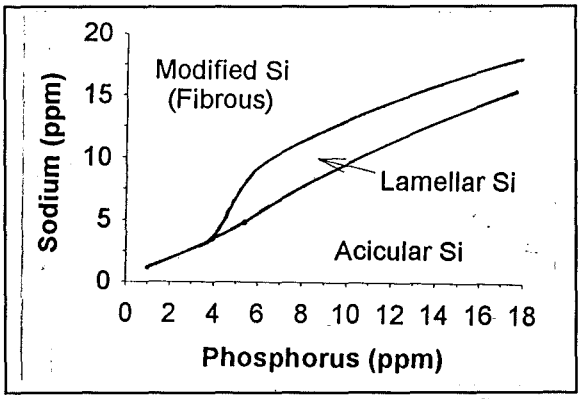

Figure 3: Al-Si7-Mg alloy, solidification time =13sec.

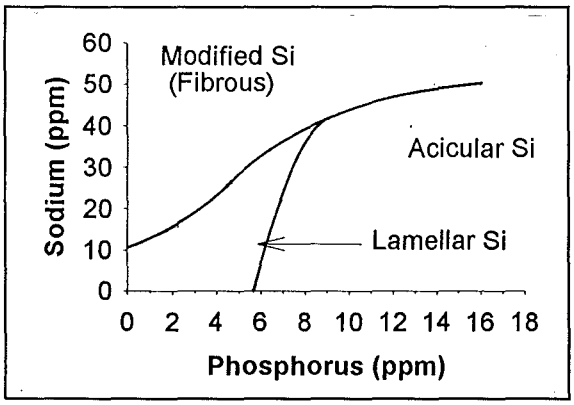

Figure 4: Al-Si13 Alloy, solidification time=13sec.

Colourimetric analysis for phosphorus was attempted by NZAS however achieving the desired accuracy of ±1ppm proved extremely difficult and time consuming. As a result the phosphorus levels present in the samples used in this research remain to be determined. A consequence of this is that it becomes impossible to differentiate between the effects on modification from an individual element and those due to phosphorus its master alloy may also introduce. It is hoped that the phosphorus levels may be established at a later date, so that more information may be gained from the modification and composition data collected.

Results

The following results are based on the outcome of preliminary multi-linear-regression analysis (MLR). Data from samples containing boron were excluded from this analysis and data for, grain size, porosity and modification rating was not yet available.

Silicon

Variation in silicon content appears to have negligible effects on the mechanical properties. This is in agreement with other published results[9] which indicate that mechanical properties vary little as silicon concentration is adjusted from 4 to 13%. The only trend which was evident from the MLR was that of increasing silicon levels having a very slight negative effect on ductility. This is most likely due to the higher silicon concentrations requiring increased modifier levels to achieve the same modification rating.

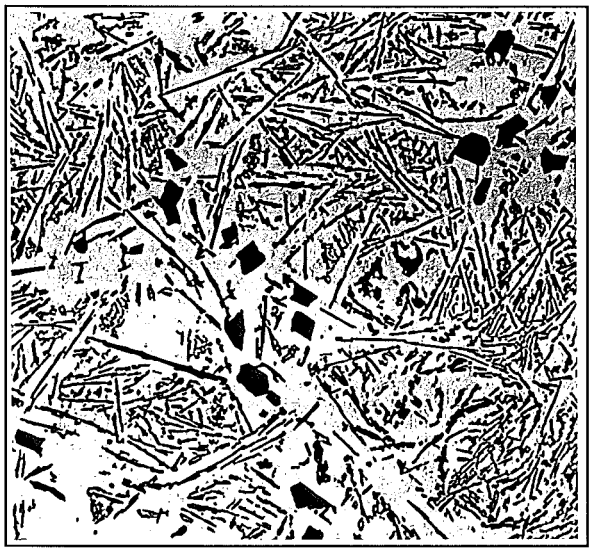

Figure 5: Unmodified LM6, (×150).

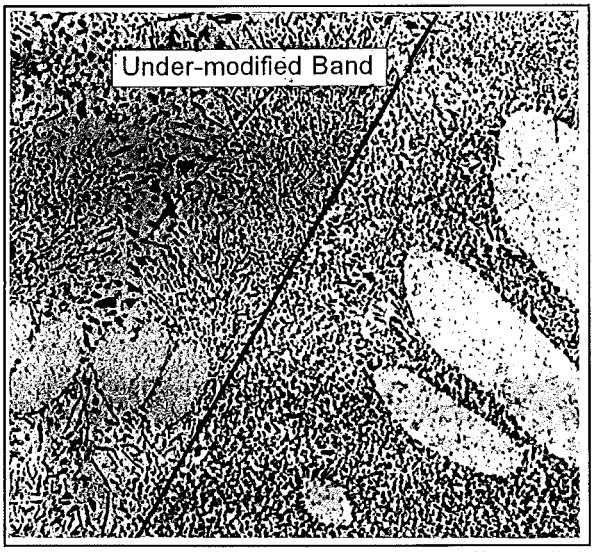

Figure 6: Strontium (L) and Sodium (R) Modified LM6, 241ppm Sr (×150).,180ppm Na (×300).

Sodium

The major states of sodium modification are shown in figures 5, 6 and 7. Adding sodium affected the mechanical properties much as expected with tensile strength and ductility peaking at around 150ppm sodium. This corresponds to the concentration at which the optimum modification rating was generally achieved. At this point strength had improved 20-25%, ductility was as much as tripled, and hardness was at its minimum. With sodium levels beyond

180ppm over-modification set in and strength rapidly decreased. This decrease continued until the sodium concentration exceeded 300ppm, where upon the tensile strength appeared to gradually increase again. When sodium levels were in excess of 250ppm the ductility decreased to magnitudes as low as that shown by the unmodified alloy, any further sodium additions continued to decrease ductility but at a far slower rate (see Figure 8).

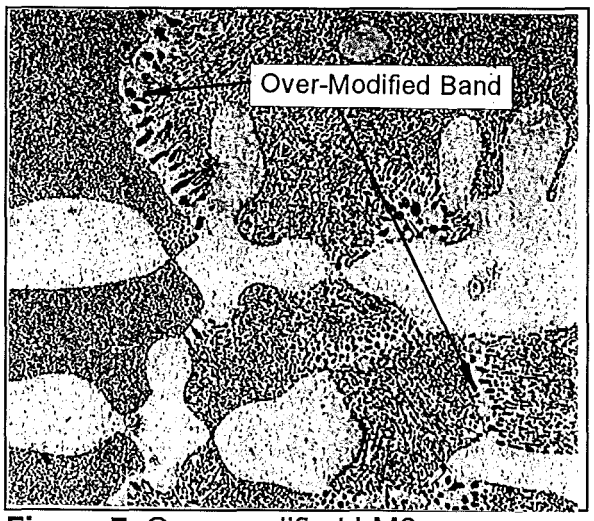

Figure 7: Over-modified LM6, 534ppm Na, (×300).

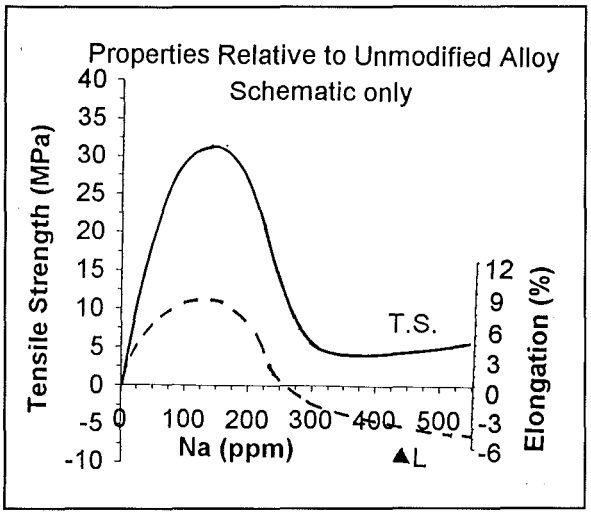

Figure 8: Sodium Modifications Effects on the Mechanical Properties of LM6.

Strontium

Strontium is often reported[2] to be less detrimental to mechanical properties than sodium when present in excess. MLR results support this but indicate a significant loss in ductility when the strontium concentration exceeds 300ppm. The gains in tensile strength with strontium modification were not as significant as those achieved with sodium, the difference between the two typically being as much as 10 MPa. This difference is no doubt due to strontium not achieving the same level of silicon refinement as sodium, as illustrated in Figure 6. The under-modification bands shown in Figure 6 are common in the microstructure of samples modified with strontium even when excessive additions are made. The optimal concentration for strontium addition was in the range 200-300ppm.

Iron

Increasing iron levels had a very minor negative effect on ductility. The only significant influence iron had upon the mechanical properties was a large increase in the proof strength, typically 12MPa when present at 0.6%. Iron was in fact the only element to significantly effect the proof strength. Figure 9 illustrates the iron needles ($FeSiAl_5$) associated with iron contamination. This image can be compared with Figure 10, which is of an alloy containing the same level of iron plus 0.514% manganese. The absence of iron needles is due to the formation of the large FeMnSiAl "script" phase shown. This phase was observed to form as primary blocks as well as script when the combined iron and manganese levels exceeded ≈0.8%. This latter block like structure is reported[4] to be highly detrimental to machinability and ductility.

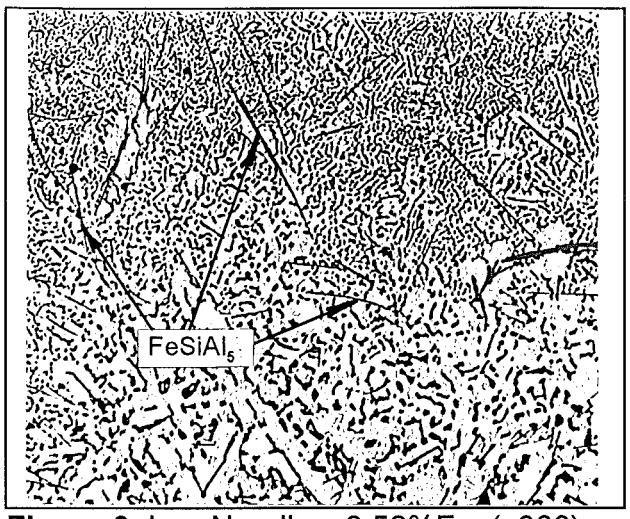

Figure 9: Iron Needles, 0.58%Fe, (×300).

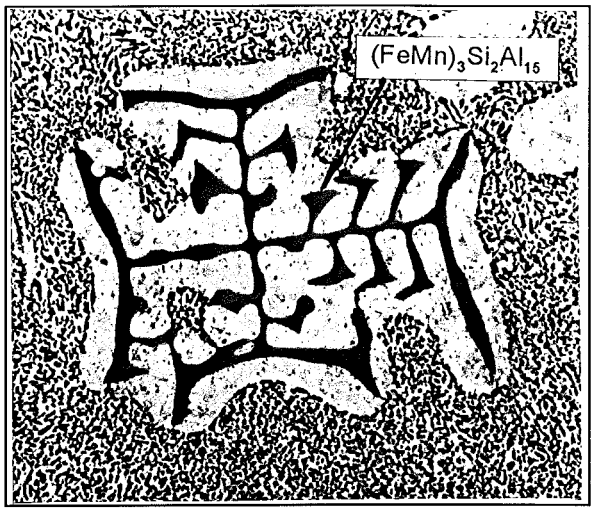

Figure 10: Large Manganese Script, 0.514%Mn, (×300).

Manganese

Increasing manganese contamination had noticeable detrimental effects on tensile strength but its affect on the other properties was insignificant. This leads to the question of whether or not iron correction by the addition of manganese is a beneficial or detrimental procedure, hopefully further analysis will help resolve this issue. An illustration of the usual chinese script AlFeMnSi phase used as an iron corrective is shown in Figure 10.

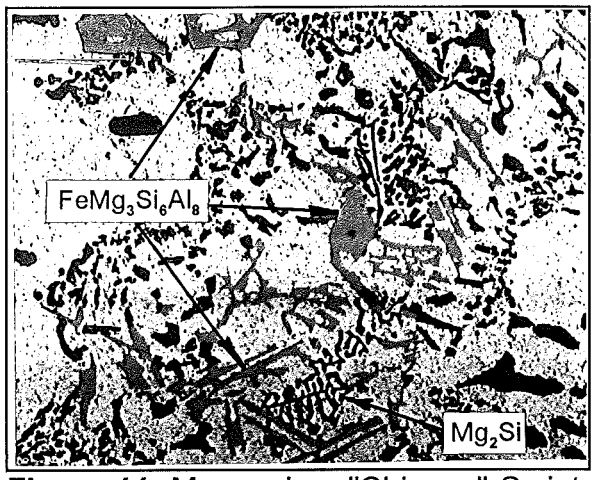

Figure 11: Magnesium "Chinese" Script, 0.101% Mg, 0.182% Fe, 0.207% Mn, (×300).

Magnesium

Adding up to 0.1% magnesium reduced ductility by as much as half, and as a consequence tensile strengths also fell slightly. The presence of magnesium also increased sample hardness, as did titanium, however the large variance associated with this property will make quantifying these gains difficult even with further statistical analysis. Figure 11 shows a microstructure typical of the magnesium contaminated samples.

Titanium

Titanium is usually added to improve the distribution of porosity via grain refinement, not to directly improve strength or ductility. However results from the MLR demonstrate very clear tensile strength improvements for samples containing appreciable levels of titanium. These strength gains were up to 10MPa when the titanium level reached and exceeded 0.05%. Figure 12 illustrates the structure of an alloy containing 0.23% titanium. The large $Ti(AlSi)_2$ needles in figure 12 were not present in alloys with less than ≈0.15% titanium. A eutectic between

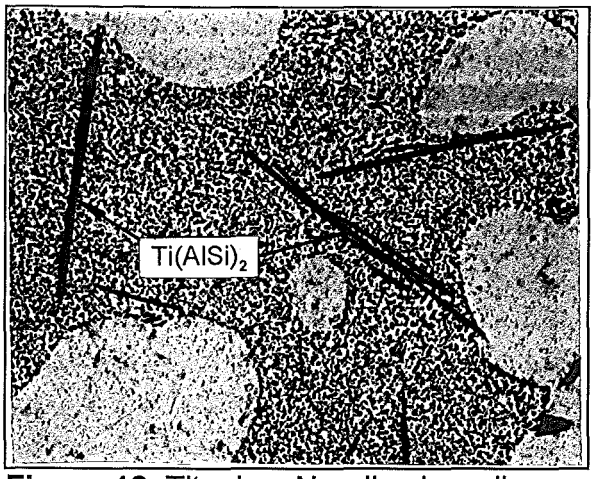

Figure 12: Titanium Needles in well modified LM6, 0.0234%Ti (×300).

aluminium and titanium is known to occur at this concentration and evidently it is not influenced much by the presence of the other elements investigated in this research.

Constituents

The identities of the phases indicated in this paper were found using an x-ray energy dispersive analyzer and the illustrations and descriptions provided in Mondolfo[4] and the "Metallographic Atlas of Cast Aluminium Alloys"[10].

Conclusion

Tabulated data now exists which will allow future multi-linear-regression-analysis to quantify the inter-relationships between almost all of the significant factors influencing the properties of cast aluminium-silicon eutectic alloys. Results to date have come from very limited statistical analysis, however they provide an interesting insight into some of the more significant relationships influencing the mechanical and physical properties. One of the more unexpected and possibly more significant results obtained is the lack of evidence confirming the widely accepted belief that iron contamination is highly detrimental to physical properties, particularly ductility. More detailed analysis of collected data will undoubtedly shed more light on this and several other important issues.

It is hoped that at a later date the levels of phosphorus present in the samples investigated will be established and incorporated into the current data, this will allow a more complete understanding of the influence this element has, not only on modification but the other properties monitored as well.

Acknowledgements

The author would like to thank the management and staff of New Zealand Aluminium Smelters Ltd for supporting this research by providing technical and financial assistance, and also for supplying large proportion of the raw materials used. Their generous support and cooperation is greatly appreciated.

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Appendix Q-(iii) IPENZ95a

The Processing of Molten Aluminium-Silicon Casting Alloys

W.D. Shilvock[1]

Abstract

The processing of Aluminium-Silicon alloys in a consistently acceptable manner requires the implementation of several critical and interdependent processes. The major processes such as degassing, modification, grain refinement and filtration are discussed. The results of two sets of experiments are also provided; the first illustrate the contamination of molten aluminium alloy due to the incorrect material selection and handling of foundry tools, the second set show the compositional effects various degassing methods have upon the eutectic alloy.

It is concluded that if New Zealand industry is to be competitive in the international foundry environment it must ensure that a complete understanding exists at all stages of production regarding the molten alloy processing steps and their effects upon the alloy in question[2].

Introduction

Ninety one and a half percent of the production from NZAS's Tiwai Point smelter is exported, this has made the smelter one of the largest exporters in the New Zealand economy. This fact is not something New Zealand's secondary industry should be overly proud of, as it represents a huge loss of opportunity to add value to one of New Zealand's most important domestic products. Casting represents possibly the single largest area in which local industry may add substantial value to large volumes of NZAS product, yet of the NZAS alloy consumed locally only one fifth is foundry ingot. For local foundries to compete internationally against products from Europe, Asia and the Americas, management and all foundry staff must have an appreciation for the theory and practice associated with modern molten metal processing.

Casting today is more of a science than a black art and involves carrying out a specific set of procedures in a controlled and pre-specified manner. A number of processes take place during the commercial casting of foundry alloy, such as degassing, modification, grain

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[2]The Author would like to thank the management and staff of New Zealand Aluminium Smelters Limited for supporting this research by providing technical and financial assistance, and also for supplying a large proportion of the raw materials used. Their generous support and cooperation is greatly appreciated.

refinement and filtration. Each of these processes has been the topic of extensive research for over fifty years and an integral part of commercial practice for almost as long. Even so, they remain the subject of much misunderstanding and scepticism both from foundrypersons and researchers alike.

Although this paper is aimed specifically at the aluminium-silicon eutectic alloy, almost all of the processes and their effects described hereafter apply equally well to most of the other common aluminium casting alloys.

The Aluminium Silicon Casting Alloys

Almost all commercial aluminium foundry alloys contain substantial quantities of silicon. The eutectic alloy is of particular relevance as it has a very low solidification temperature and an extremely narrow temperature band over which solidification takes place; this imparts the alloy with exceptionally good castability. The low solidification temperature as illustrated in the phase diagram (Fig. 1) means casting can take place at a relatively low temperature whilst thin wall and complex shapes can be produced without the incomplete mould filling associated with most other aluminium alloys. The suppressed solidification temperature and presence of large volumes of silicon phase also reduces shrinkage allowing tighter dimensional tolerances, less final machining and less waste in the form of gates and risers. The other major advantages of the eutectic alloy are its exceptional lightness - it is in fact the lightest of the common alloys - and outstanding resistance to corrosion. These factors, as well as moderate strength and ductility without the need for heat treatment, make this alloy useful in a wide range of applications from marine castings weighing several hundred kilograms to household artifacts of a few grams.

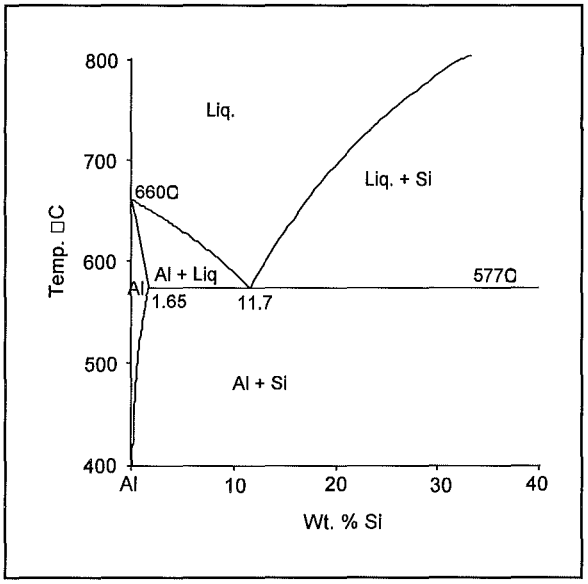


Figure 1:Al-Si Phase Diagram.

Secondary Metal

The most common specification used when ordering eutectic aluminium silicon alloy in New Zealand is British Standard 1490 grade LM6. The LM6 standard is in fact quite wide ranging in its composition specifications and permits from 10 to 13 percent silicon and up to 0.6 and 0.5 percent iron and manganese respectively. This is a specification easily attained by secondary metal producers and so LM6 is available from a number of suppliers with quite substantial levels of impurity including iron, manganese, zinc and copper. This can pose a problem to the founder because secondary alloy usually varies considerably in composition from one batch to another, and these changes in composition within the LM6 range can drastically change the response of the alloy to the treatments performed upon it. Therefore consistency is virtually impossible to achieve unless a sound understanding exists between the metal producer and the founder that very specific limits on composition variation must be maintained.

Metal Casting and Processing

Reliably achieving the physical requirements of the LM6 standard necessitates that the base stock composition be controlled, and that the processing of the alloy within the foundry be performed following specific procedures dependent upon the actual alloy being processed. The general metal processing procedure is shown in Fig. 1. Each of the steps shown provides a potential source for contamination, be it from residual cutting fluid, foundry tool erosion or low quality addition alloys. More harm than good can result if any one of these steps is performed incorrectly.

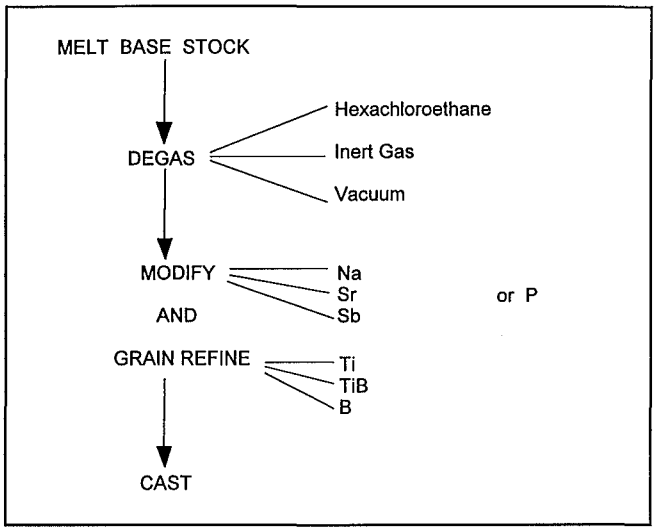


Figure 2 General Casting Route.

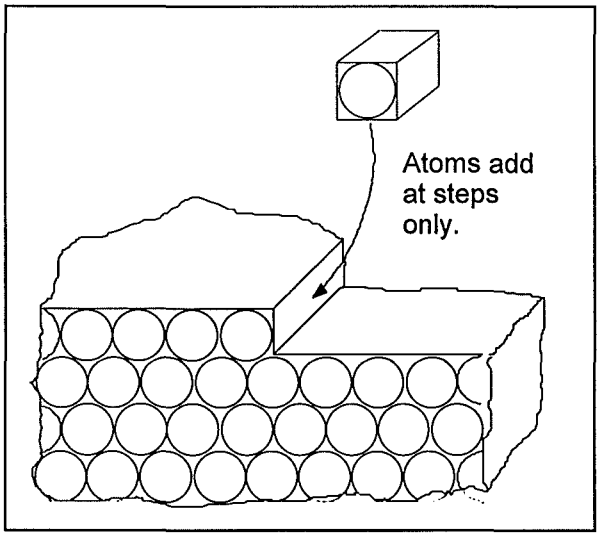


Figure3: Faceted Solidification of Silicon.

Modification

When aluminium-silicon alloys solidify the silicon forms a phase which is very nearly pure silicon; this solidifies in what is know as a faceted manner. As shown in Fig. 3, the dissolved silicon atoms present in the liquid bond on to the solid silicon phase at specific sites such as steps in the crystal surface. This results in the formation of very regular and distinct plates and blocks of silicon. These very large plates have an effect almost analogous to that of graphite in grey cast iron, in that they produce extreme brittleness and limit the ductility causing premature failure before the required strength is attained.

When modifying elements such as sodium, strontium or antimony are added to the melt, even in very small amounts, they cause a progressive refinement of the silicon and change the morphology from plates to inter-connected fibres. This is accompanied by a significant increase in ductility and hence strength. The most powerful of the modifiers is sodium which is required in smaller amounts than either strontium or antimony, and produces a structure finer than that possible with any other modifier. The modifying elements achieve this drastic change in the solidifying silicon's behaviour by bonding to the addition sites and disrupting the crystal structure. This produces very high levels of twinning which in turn allows the silicon to branch out in several directions forming a much finer interconnected network of small plates or fibres.

If excessive amounts of sodium are added then a AlSiNa phase will form which acts as a very strong nucleant of silicon, this causes the formation of moderately coarse silicon particles along the solidifying front. After some growth of this silicon, the liquid is aluminium rich and aluminium is nucleated leaving a very distinct band of coarse silicon, followed by a small band of aluminium. This over-modification is accompanied by a substantial drop in strength although it is preferable to have minor amounts of over-modification than not to modify at all.

Over-modification with strontium is also possible, this results in the formation of Al_4SrSi_2 phase and a coarsening of the silicon. Kanicki[1] reports that "over-modification and its resultant detrimental effects on mechanical properties are a major concern with sodium but not with strontium". Rauta[2] states that "excessive additions of strontium do not cause aluminium banding or silicon coarsening. However undesirable SrSi and $SrAl_2Si_2$ have been observed". It has also been indicated by Kawecki-Billiton[3] that evidence exists to show strontium will reduce the embrittling effect of the FeSi phase, such a phenomena is not reported for the other modifiers.

When strontium is used as the modifier it is usual to purchase pre-modified ingot and for no further modification to take place in the foundry. This is due to the fact that strontium is sufficiently stable within the melt to last through remelting and degassing, *provided reactive gases are not used during degassing*. Sodium on the other hand is relatively unstable in the melt and so must only be added after degassing in the casthouse. Some sodium may well be present in an initial charge due to recycled scrap and reject castings, however as is shown later in Fig. 11, negligible amounts of this will survive degassing irrespective of the method used.

Figure 4: Unmodified LM6, (×100).

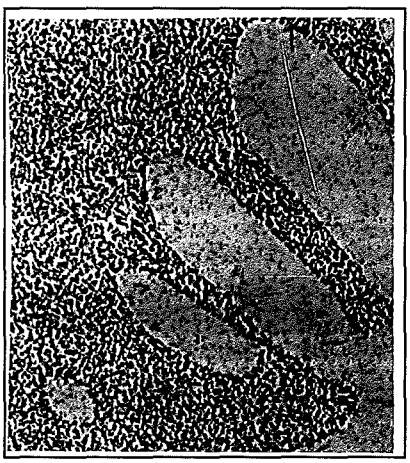


Figure 5: Modified LM6, (×200).

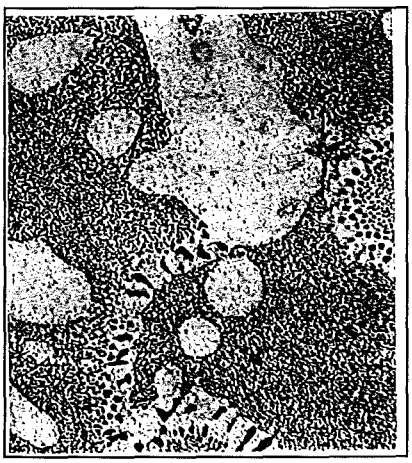


Figure 6: Overmodified LM6, (×200).

The main states of modification are shown in Figures 4 through 6.
It should be noted that refinement of the silicon phase is possible by increasing the cooling rate, and if permanent metal moulds are used it is often possible to achieve quite acceptable physical properties without the need for complete or even partial modification. The increased chilling rate does not change the shape or nature of the silicon, only its size, so modification can still result in further substantial improvements in the physical properties of the cast alloy.

Degassing

As shown in Fig. 7 the solubility of hydrogen in aluminium increases rapidly with temperature. Upon cooling and solidification this dissolved hydrogen will come out of solution in the form of bubbles resulting in porosity. Natural degassing by holding the melt at low temperature prior to casting is too slow to be of commercial significance. Hydrogen pick up by the melt is unavoidable but can be reduced by minimising any moisture or hydrocarbon sources present, particularly those associated with incompletely cleaned and dried, base metal, tools or crucibles.

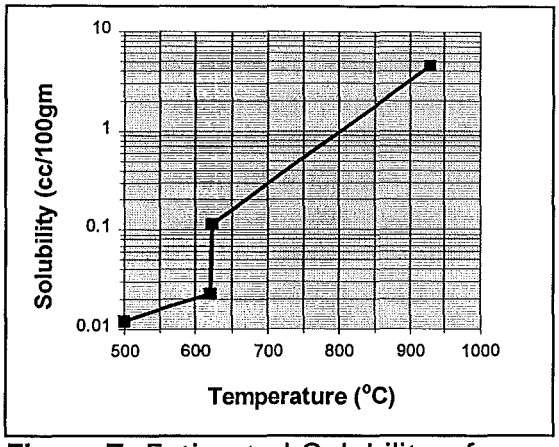


Figure 7: Estimated Solubility of Hydrgen in LM6.

There are several degassing methods which facilitate the removal of hydrogen from the melt prior to casting. All of these methods use one of three basic mechanisms. The least common of these is vacuum degassing which involves drawing off the hydrogen by exposing the melt surface to a reasonably high vacuum. This method is in commercial use in some of the larger foundries in Europe and the United States but is not used by smaller foundries as found in New Zealand.

The second mechanism involves introducing a reactive gas such as chlorine or fluorine to the melt. Bubbles of these gases react with the atomic hydrogen present and rapidly strip the melt of excessive gas. The reactive gases are usually introduced via decomposing tablets such as hexachloroethane or by direct injection. When direct injection is used the reactive gas is usually mixed with argon or nitrogen. Direct injection of the gases can be achieved using ports within the furnace base, lances or submerged rotary impellers. Degassing efficiency increases with a decrease in bubble size and one of the most efficient methods of achieving a fine dispersion of bubbles is to use a submerged porous impeller.

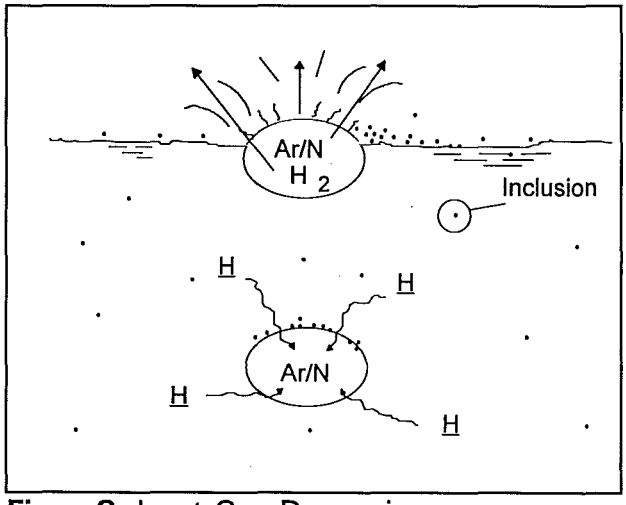


Figure8: Inert Gas Degassing.

An increasingly popular method of degassing is to introduce an inert gas such as argon or nitrogen. As shown in Figure 8, bubbles of these gases provide a medium into which the atomic hydrogen will diffuse. The bubbles then float to the surface to release the hydrogen into the atmosphere. Figure 8 also illustrates how the bubbles of gas help flush any suspended oxides and undissolved media to the surface so that it may be integrated into the surface dross.

Degassing Lance Requirements

Figures 9 through 11 illustrate the results of a set of experiments designed to highlight the contamination of a melt by the degradation of degassing lances. The results also highlight the effectiveness of alumina type coatings such as Abel-Lemons "Alcoat D" in protecting exposed materials in contact with the molten aluminium.

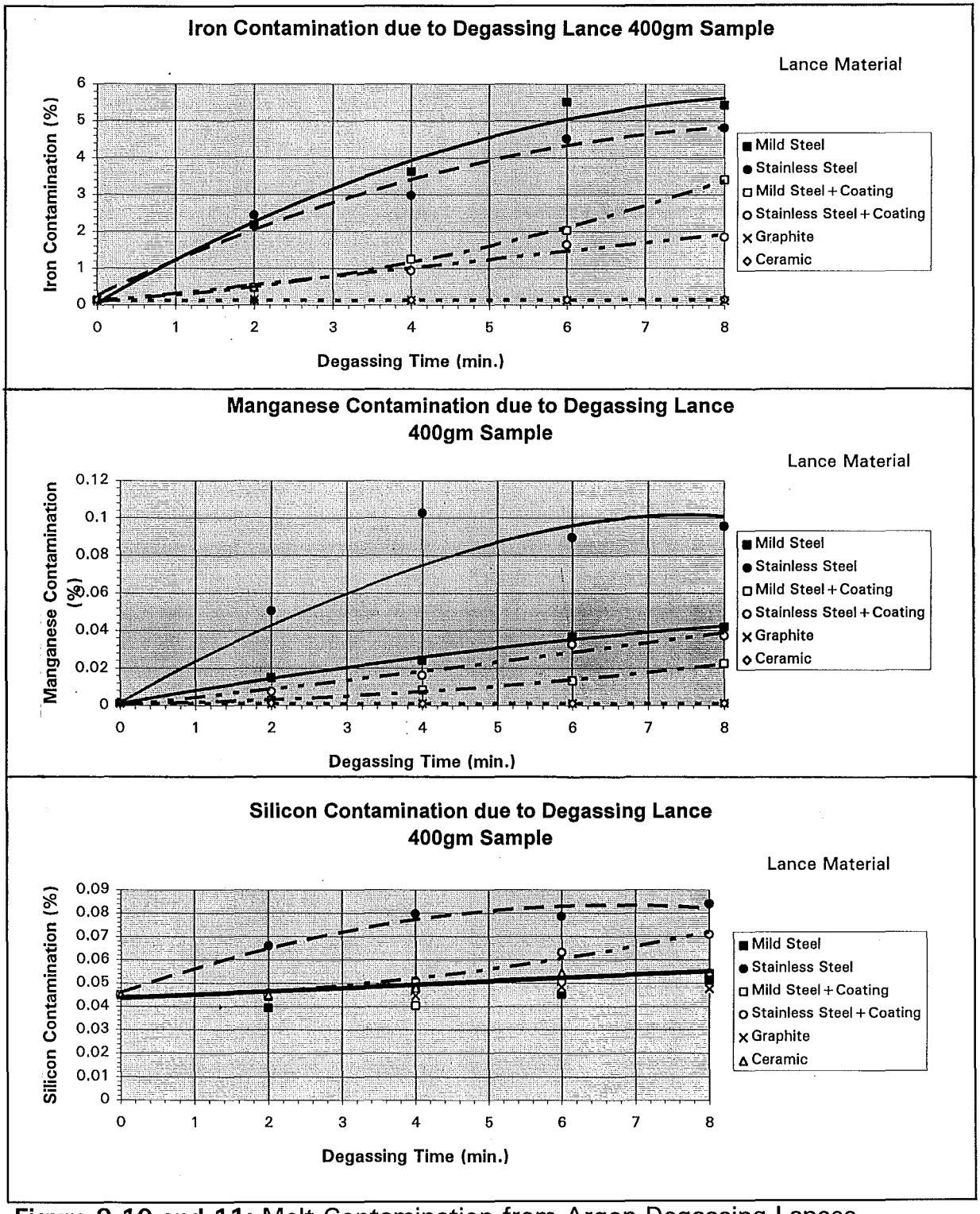


Figure 9,10 and 11: Melt Contamination from Argon Degassing Lances

These experiments were performed by exposing small quantities of high purity aluminium (400g) to large argon lances (approx 12mm O.D.) at a constant temperature of 780°C. Consequently these results overstate the level of contamination which could be expected commercially, however they do provide a clear indication as to the suitability of the various lance materials used.

It should be noted that although the alumina coating proved its worth by reducing contamination by 50-60 percent the only really acceptable materials used were the ceramic (in this case a mullite type) and graphite. The current high costs associated with ceramics capable of reliably withstanding 700-800°C thermal shock loadings, restricts their use mainly to areas other than commercial foundry tools.

These results highlight how much caution must be exercised when exposing conventional materials to highly reactive molten aluminium.

Impurity Removal by Degassing

It has long been known that degassing will aid the removal of inclusions as well as some alloy elements, the modifiers being particularly sensitive in this regard. A set of experiments has consequently been carried out to investigate which elements are removed and their rates of depletion. The experiments involved melting a 4kg charge of eutectic alloy and then monitoring the metal composition as degassing took place. The alloy was initially boosted to the maximum permissible levels of magnesium, manganese, zinc and iron. The grain refiners titanium and boron and either sodium or strontium modifier were also added in amounts typical of those found commercially.

The degassing methods used were lance injection of either argon or nitrogen, or tablet additions of chlorine or nitrogen. Experience with similar size melts and lance injectors has shown comprehensive degassing to take less than five minutes. The nitrogen degassing tablets (Foseco Degasser 610) are specifically designed to be used with strontium premodified ingots so as to minimise modifier removal and eliminate the need for inert gas hydrogen purging equipment. Hence these tablets were only used when strontium was used as the modifier.

It should be noted that the chlorine tablets used (Foseco Degasser 190) are also sold as grain refiners hence it was surmised that they would not cause the removal of titanium or boron at the same rate as the other processes investigated.

The level of variation in composition for the major impurity elements affected are illustrated in Figures 12 through 21.

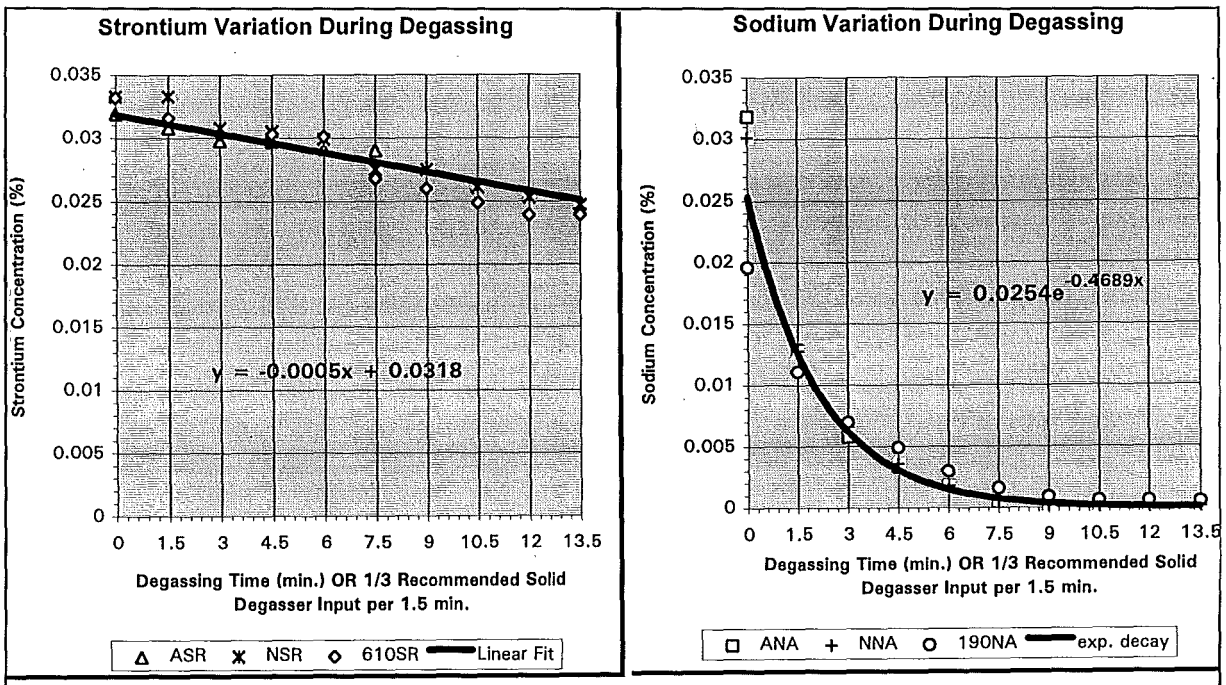
Points to be observed are:-

- The very rapid removal of sodium was independent of the type of degasser used. This can be directly compared with the very gradual extraction of strontium.
- The formation of NaCl is thermodynamically far more favourable than $MgCl_2$, consequently sodium should be removed before magnesium as indicated by Neff[4]. However figures 20 and 21 show that magnesium is removed far faster in the presence

of either sodium or a reactive gas. This supports the practice of not using sodium salt cover fluxes on alloys containing magnesium if the level of magnesium present is to be retained.

- Silicon is removed faster in the presence of sodium. This may be due to the formation of $(NaAl)Si_2$ and the silicon being extracted with the sodium rather than the precipitate breaking down.
- Silicon does not appear to be removed faster in the presence of magnesium, even though the magnesium is likely to be present as Mg_2Si or $FeMg_3Si_6Al_8$.
- Both the titanium and boron concentrations fell significantly irrespective of the degassing method used except ....
- The degasser 190, which is promoted as a grain refiner and degasser did appear to promote the retention of boron levels, but had little if any effect on the level of titanium remaining in the melt.

It must be concluded from this work that degassing methods should not only be selected dependent upon the initial alloy composition but the degassing times and amount of returned feed stock must be closely monitored, otherwise maintaining product composition and hence physical consistency becomes virtually impossible.



Note: A 10 minute reheat of these casts took place after 6 minutes degassing.

A_ _ = Argon degassed.

N_ _ = Nitrogen degassed.

_NA = Sodium added as initial modifier.

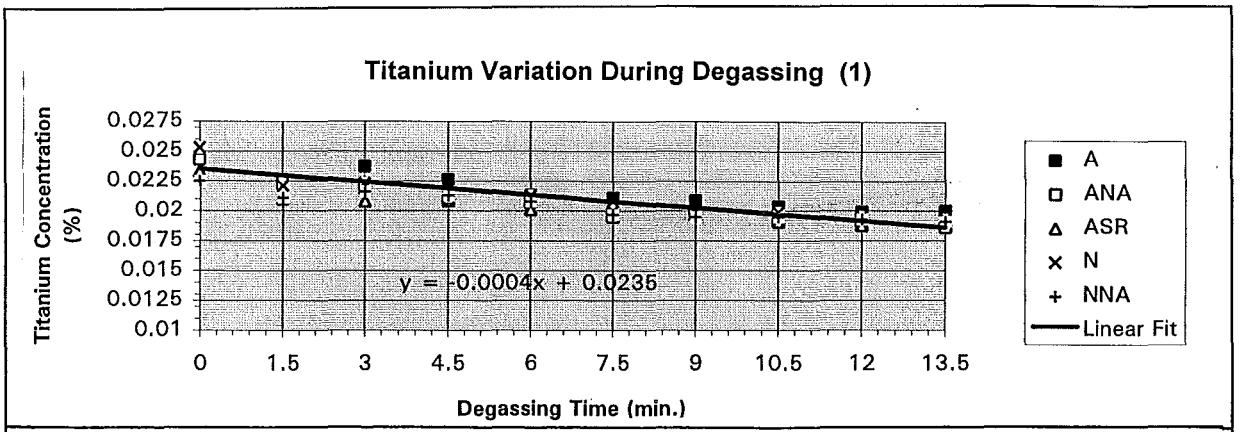
_SR = Strontium added as initial modifier.

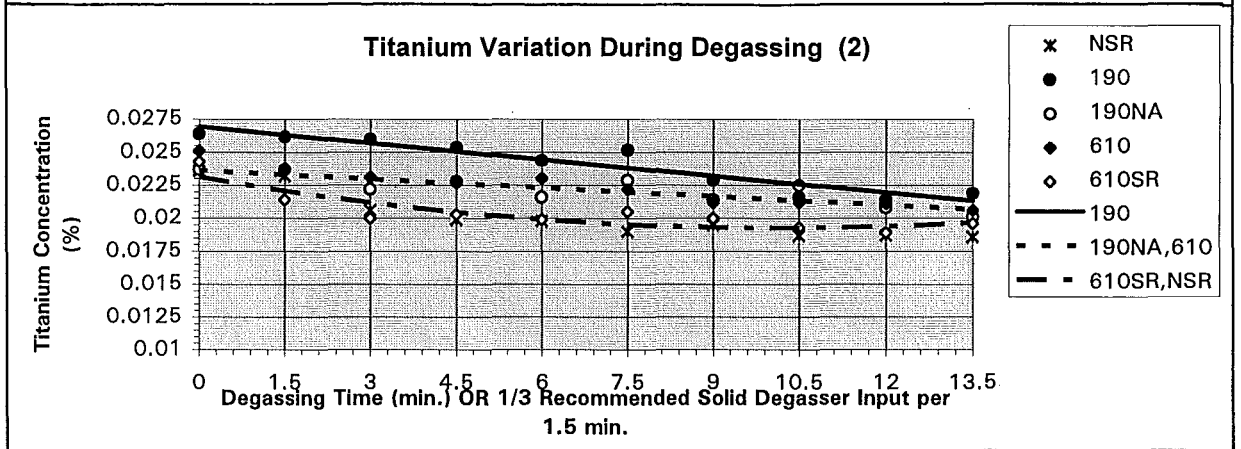
190_ _ = Foseco "Degasser190" degassed - This product uses Chlorine as the purging gas and also acts as a grain refiner.

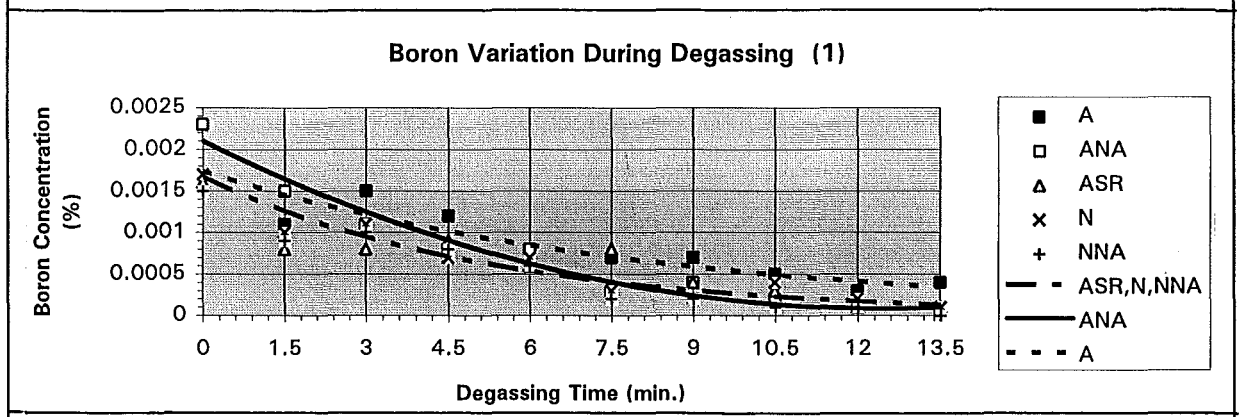
610_ _ = Foseco "Degasser 610" degassed -This product uses Nitrogen as the purging gas and is designed specifically for use with Strontium premodified ingot.

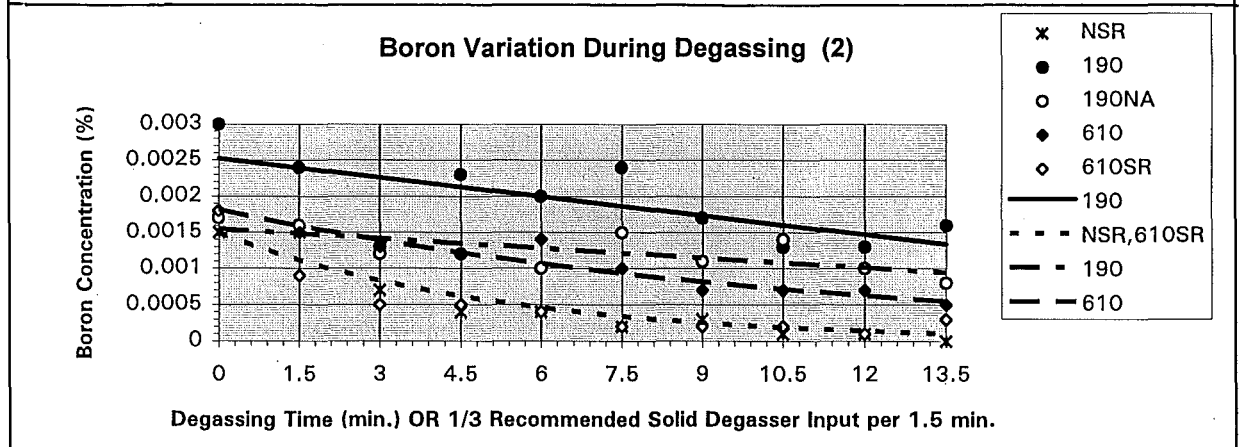
Gas flow rate used = 2.4l /min. (0.142m^3/Hr.).

Figures 12 and 13: Modifier Removal Due to Degassing



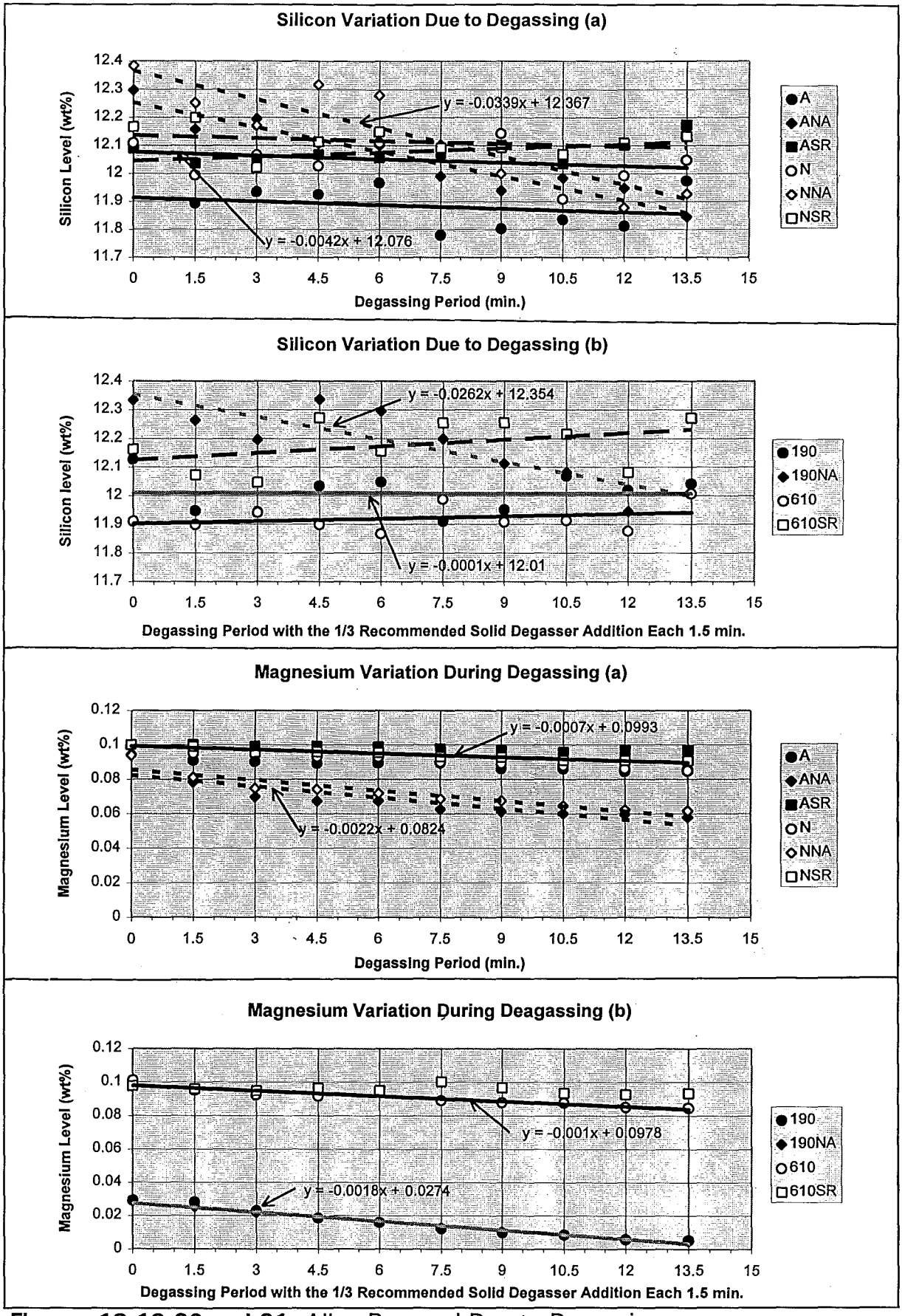






Note: A 10 minute reheat of these casts took place after 6 minutes degassing.

Figures 14,15,16 and 17: Grain Refiner Removal Due to Degassing



Figures 18,19,20 and 21: Alloy Removal Due to Degassing

Grain Refinement

Al-Ti and Al-Ti-B grain refiners have been in widespread commercial use for many years. Despite countless investigations the mechanisms behind the refining processes are still poorly understood and scepticism surrounds the practical worth of this treatment. The ability of certain elements to achieve grain refinement is beyond question, however any mechanical advantages resulting from the grain-refinement of high silicon alloys are reported to be minimal to non-existent. Vass[5] states "the mechanical properties obtained do not appear to be significantly effected by the titanium level, the amount of the addition or the grain size", an opinion which is shared by Sigworth[6]. There is agreement that a fine grain size reduces the size of porosity present, resulting in a fine dispersion of voids rather than a few large pores. This is reported to have little effect on the mechanical properties other than to improve the consistency of results; in other words better mechanical properties can not be expected but less variation between melts and within castings should be encountered. It is also generally accepted that the grain-refined metals' ability to disperse porosity greatly assists casting soundness, particularly with large castings.

Figure 22 (from[7])illustrates the effects of various grain refining master alloys on commercial purity metal. It can be seen that fade is quite a problem when pure titanium is added(a) but additions of boron(b and c) greatly increase the period over which refinement lasts. It must be stressed that the response of a master alloy is extremely dependent upon its thermal history, not just its composition. Titanium dissipates into the melt as $TiAl_3$ which is an extremely effective nucleant of aluminium requiring very little undercooling. It is normal practice to add around 0.01 - 0.02% titanium, however a peritectic reaction occurs at 0.15% titanium causing the $TiAl_3$ to dissolve, the result being that titanium refinement is subject to

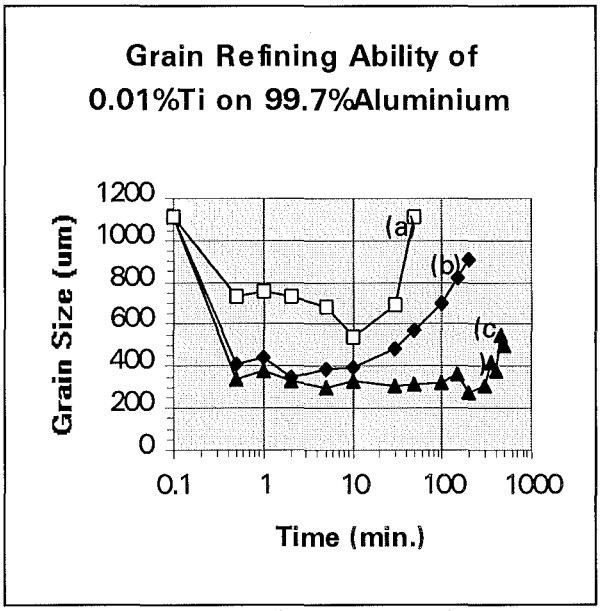


Figure22: a = 5.35%Ti, b = 5.4% + 0.034B c = 5.0%Ti + 0.2%B

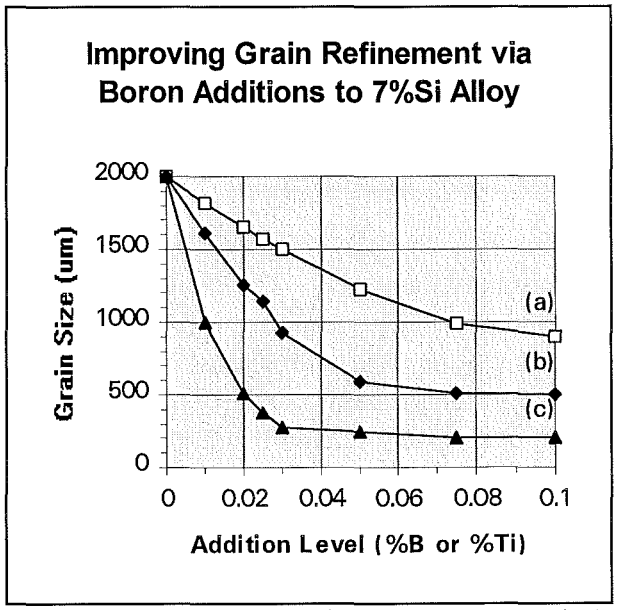


Figure23: a = Al + 5.0%Ti, b = Al + 5.0%Ti + 1.0%B, c = Al + 4.0%B

fade as shown above. Numerous theories regarding how boron reduces this fade have been proposed but Guzowski, Sigworth and Sentner [8] propose what is possibly the most complete explanation. They noted that grain refinement is most effective when borides are attached directly to the titanium particles. From this they proposed that the titanium rich regions

surrounding the titanium sites, even following the titanium's solution, promote undercooling to the point where AlB_2 can act as a nucleant. This necessity for undercooling makes boron alone totally ineffective in the refinement of purer alloys. However this is not the case with alloys displaying suppressed solidification temperatures as is the case with the eutectic alloys and others containing appreciable amounts of solute. Although it is not commercial practice to use boron alone, boron has been shown[7] to promote a finer grain size than the titanium or titanium-boron mixes. This can be seen in Figure 23 (from[8]). An illustration of the degree of grain refinement gained with the eutectic alloy is shown in Figure 24.

Filtration

Filtration to remove oxide and other insoluble contaminants within the melt has become an integral step in the production of high quality castings. These contaminants not only directly reduce strength, ductility and fatigue resistance but also entrap substantial pockets of gas. It is stated by Clegg[9] that the oxide also acts as a reservoir for hydrogen even after comprehensive degassing, hence their association with unwanted porosity.

Modern filters are generally made from alumina and may be used at any step in the metal transfer process, but the most common and effective position is in the mould feeder. In the mould they not only filter but cut down turbulence during mould filling and this in itself reduces oxide entrapment as well as mould erosion. One of the major achievements of the in-mould filter is to remove large titanium and boride particles which may have been introduced via excessive or low quality grain refiners. The coarse grain refiner particles along with any carbides present greatly reduce melt fluidity and produce "hard spots" within the casting. The nett effect of these, and the oxides upon secondary manufacturing operations is to greatly reduce cutter life and increase scoring due to swarf pickup.

Effective filtration when carried out by ceramic filters embedded in the mould feeders has been reported to cut casting rejections by as much as 90%[10].

Cover and Cleaning Fluxes

Fluxes based on the NaOCl-KCl system are widely used as covers and cleaning agents in most aluminium foundries. The NaOCl - KCl salts melt and form a molten layer on top of the aluminium, thus protecting it from both oxidation and reaction with moisture. While most fluxes can be used with almost any alloy those containing sodium salts are not recommended for high magnesium alloys. The reason for this is that magnesium tends to be displaced by sodium resulting in significant losses of magnesium to the dross. When magnesium alloys are used it is usual to apply a flux based on the $MgCl_2$ - KCl system.

The cleaning action associated with most cover fluxes comes about by the addition of sodium flurosilicate ($Na_2Si\ F_6$). The flurosilicate effectively coats the aluminium oxide layer allowing turbulence to mechanically strip away the oxide from its aluminium core the oxide will then float to the surface and be removed with the dross. The traditional method for adding fluxes is to manually apply salts to the melt surface, then to rabble them in so that they may react with any oxides present. The alternative method is to use flux injection and blow flux into the melt through an inert gas lance. This combines degassing and fluxing into one step and allows the flux to react throughout the entire melt rather than just within the surface region.

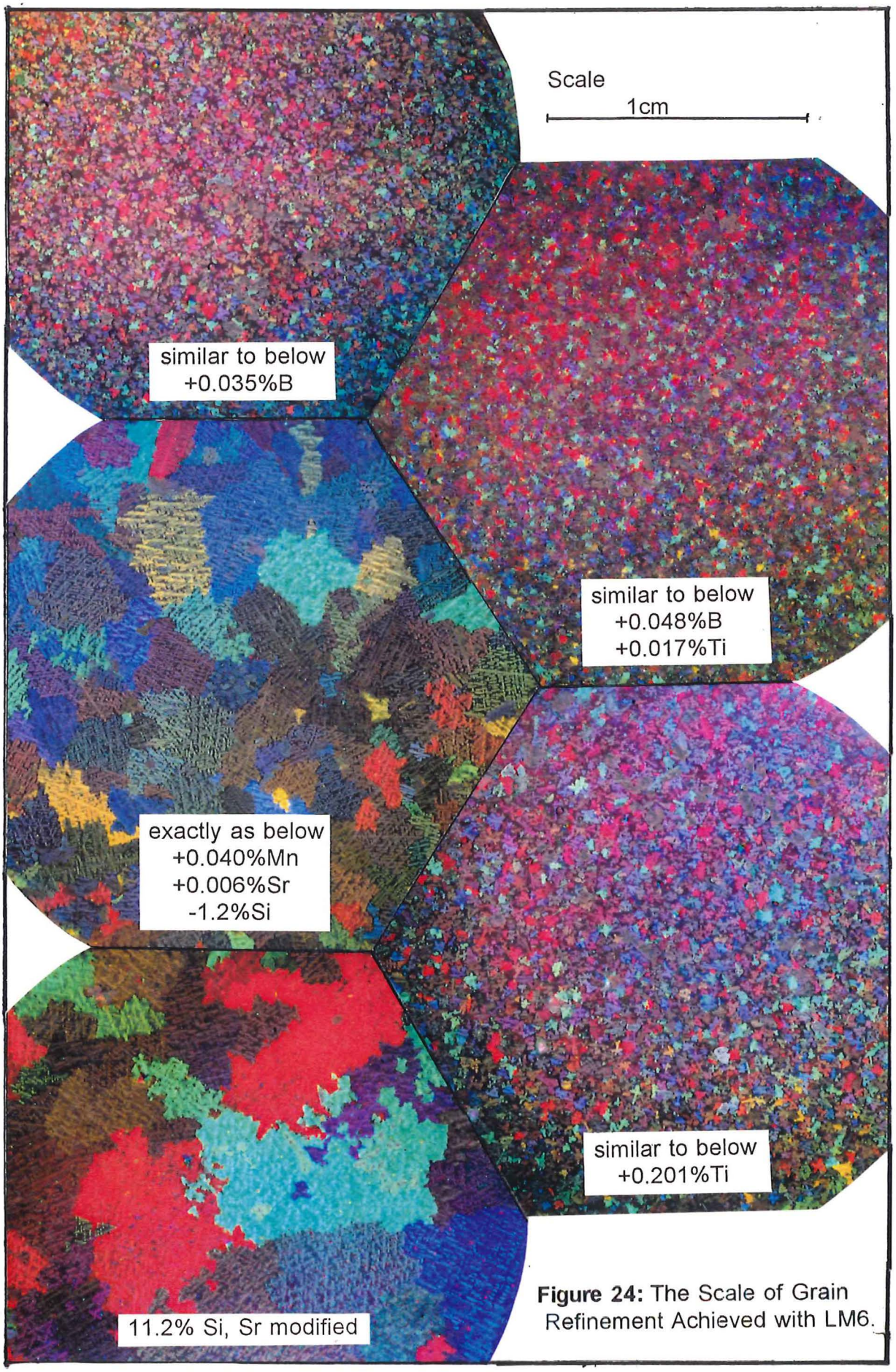


Figure 24: The Scale of Grain Refinement Achieved with LM6.

Conclusions

The main conclusions to be drawn regarding the casting of aluminium alloys and in particular the eutectic alloy are:

- If the required physical standards of BS1490 LM6 are to be consistently surpassed by a reasonable margin then foundry management and staff require a complete understanding of the mechanisms and full effects of all of the processing steps which take place.
- Implementation of stringent base metal and additive standards regarding initial composition and subsequent handling are just as vital as consistency in the processing steps themselves.
- Contamination from sources such as the surface oxide layer and foundry equipment must be reduced as much as practicable.

Finally, the choice of processing route and additives to be used must be made knowing the exact characteristics of the alloy in question and the application (eg mould size and type) for which it is being used.

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Appendix Q- (iv) IPENZ95b

The Physical Effects of Common Impurities Present in Aluminium-Silicon Castings

W.D. Shilvock[1]

Abstract

Interrelationships between the bulk of the impurities commonly found in aluminium-silicon castings and the mechanical and physical property variations they cause remain largely unquantified. This paper outlines a set of experiments performed at The University of Canterbury with the aim of resolving this issue for at least the most common impurities. The composition and physical properties of approximately 500 different cast samples were monitored and the results subject to Multi-Linear-Regression (MLR) analysis. This paper deals with MLR results indicating significant trends such as the gains in strength attributable to titanium addition, contrary to what has been widely reported. Due to space considerations only the tensile test properties of ductility, proof strength and ultimate tensile strength are covered.

Introduction

The aluminium-silicon eutectic alloy has been one of the most important aluminium foundry alloys in use since 1920 when Pacz discovered that the solidifying silicon phase could be refined by a process known as modification. Since that time several other procedures have been adopted as integral steps in the casting of this alloy, such as; degassing, filtration and grain refinement. Countless investigations have been carried out into each one of these processes, however one thing that comes to light very quickly is that these investigations have almost always been performed from a metallurgical perspective. That is they have set out to establish why and how the processes work as opposed to quantifying the physical significance of variation within each melt treatment.

Very clear standards exist regarding how to quantify the various states of modification. The point at which modification ceases to be physically advantageous, and over-modification with its associated detrimental effects begins is also well established. Even so no clear guidelines exist quantifying the change in mechanical properties that can be expected due to variation in the level of modification. There is also very little information, quantitative or otherwise, regarding the effects impurity elements have on modification, grain refinement or porosity, with the obvious exception of the modifying and grain refining elements. Gruzleski[1A] makes note of this point

[1] Postgraduate Student, Mechanical Engineering, The University of Canterbury.

and draws attention to the fact that most of the published information to date has been contradictory.

It should be noted that BS1490-LM6 is the most common specification used in New Zealand when referring to the Aluminium-Silicon eutectic casting alloy. Other commonly used designations include Australian Standard 1874-401 and ISO 3522 Al-Si12. The tensile properties required by these standards for the sand cast LM6 type alloy are a tensile strength of 160MPa and a minimum elongation of 5%.

Controversy surrounds several common practices associated with the aluminium-silicon alloys, such as the addition of manganese to reduce the embrittling effects of iron. This practice relies on the removal of $FeSiAl_5$ needles present within the eutectic by the formation of $(FeMn)_3Si_2Al_{15}$ which usually appears in the shape of Chinese script within the primary aluminium dendrites. It is well established that these structures do form, however their effects on the mechanical properties is still open to debate, particularly with reference to the alloy in question. Detailed investigations[2] on AlSi7Mg casting alloys have shown that the embrittling effect is more pronounced in chill castings than sand castings, and that it shows up far more clearly in impact tests than by conventional tensile testing. It is also widely reported[3][4] that excessive levels of iron are directly detrimental to ductility, something that previous studies at The University of Canterbury[5] have failed to substantiate.

Experimental Procedure

The impurities and their composition ranges to be investigated were selected so as to be as wide ranging as possible yet within the LM6 standard. The elements singled out for investigation were chosen because they are routinely found in locally processed eutectic alloy, particularly when secondary base metal is used. Zinc was not included in the investigation as it is well reported[4] that its influence on room temperature properties is minimal when present in concentrations as high as ten times that permitted by the LM6 standard. The final composition variables used are shown below along with the ranges in which they were cast.

Silicon	10-11.5-13%
Iron	0-0.6%
Manganese	0-0.2-0.5%
Magnesium	0-0.1%
Sodium	0-(0.015)-0.05%
Strontium	0-(0.025)-0.05%
Titanium	0-0.2%
Boron	0-0.05%

The values in brackets represent the typical modifier additions made.

Specific concentrations of each element were aimed for, these values usually being the limits listed above. However experimental scatter resulted in a range of compositions being produced covering the entire composition spectrum.

Casting Procedure

Where possible all processes and equipment used during casting were designed to model commercial foundry practice. All casting was carried out utilising a gas fired furnace, conventional clay/graphite crucibles and low carbon steel foundry tools. All tools and crucibles were coated in Abel-Lemon "Alcoat D", an alumina based refractory, this reduced melt contamination and prolonged tool life. Upon the completion of casting some material loss from the tools was evident, however the amount was minimal considering that 270 melts had been made.

Melt sizes varied from 1.1kg if a single specimen was cast, to 4kg when four specimens were to be produced. All test bars were cast using identical sand moulds supplied by C.W.F. Hamilton Ltd and complying to B.S. 1490. At the same time composition disks were cast for later spark emission analysis at New Zealand Aluminium Smelters Ltd, the analysis providing composition results for 21 elements including all of those mentioned above. The base material used during casting was NZAS CA401F, an aluminium-silicon eutectic alloy routinely supplied to the domestic market. This alloy was supplied unmodified with minimal impurity other than an iron level of 0.18%. Where necessary the silicon levels were reduced by the addition of commercially pure aluminium, while the levels of most other elements were adjusted by the addition of commercial master alloys, the exceptions being magnesium and sodium which were added directly as pure metal. The addition of boron was carried out using two master alloys one containing 5% titanium 1% boron and the second being 3% boron. Particular care was taken when ordering the 3% boron master alloy to ensure the alloy contained predominantly AlB_2 and not AlB_{12}, as the more common AlB_{12} is supposedly not an effective grain refiner. Unfortunately upon completion of casting the supplied 3%B alloy was found to be of the AlB_{12} type. This master alloy has subsequently proven to be an effective grain refiner contrary to what may have been expected.

As is normal practice melts were not allowed to exceed 800°C and modification took place following degassing in the range 720-740°C. All final pouring was carried out in the temperature range 700-720°C

Degassing

Degassing was performed by injecting pure argon into the melt via a graphite lance. Low pressure tests (Straube-Pfeiffer tests) revealed that comprehensive degassing of the base material (CA401F) had taken place after five minutes. This degassing time was subsequently used for all melts irrespective of the amount of porosity being observed in the final castings. This was done so that any increased porosity, due to shrinkage or gassing, could be related back to the impurity additions made.

When inert gas degassing is performed commercially nitrogen is used as the gas medium, however for these experiments argon was chosen. The reasons for using argon were, the availability of certified high purity gas to minimise contamination when supply pressures fell and the availability of alternate gas supplies should they be required during melting. The similarity in the way argon and nitrogen perform was demonstrated in degassing experiments detailed in a previous paper, consequently it is considered unlikely that the use of argon instead of nitrogen would have effected the final test piece properties.

Fluxing

Early melts had fluxing covers applied in the form of Foseco "Coveral 11". However, this process was not continued due to contamination of test bars by particles of cover and dross. This was brought about by a build up of flux forming on the crucible wall which was extremely difficult to extract and tended to be dislodged during pouring. It is unlikely that this problem would be encountered when melting larger volumes of metal, as the crucible would be far easier to clean and the amount of flux added per kilogram of metal melted would be substantially lower.

Physical Testing

Tensile Testing

All cast tensile test specimens were machined and then tested in accordance with B.S.18. The samples had a diameter of 11.28mm and were tested on a computerised Satec Universal Testing Machine. This provided tensile strengths, 0.2% proof strengths, elongations to failure and stress strain curves. Typical tensile properties are listed below...

	Unmodified	Na Modified
UTS (MPa)	115	165
0.2%PS (MPa)	88	92
δL (%)	5	10

Hardness Testing, Modification Rating, Grain Size and Porosity Level.

All of the samples cast were subject to hardness, modification grain size and porosity analysis. Samples were hardness tested using Hv_{10} in accordance with B.S.427. To compensate for variation in hardness across the test piece diameter six hardness tests were performed in a traverse across each sample. The modification rating for each sample was established using standard AFS(American Foundrymen's Society) modification scales[6], and then multiplying each scale value by the proportion of the sample area which it represented[1B]. Grain size was quantified by one of two methods, if the grains could be highlighted and distinguished easily they were visually rated using standard ASTM Macro Grain Size plates, if the grains were not equiaxed or clearly distinguished then the Jeffries method as described by ASTM was used. The methods of modification and grain size measurement are briefly described in the accompanying paper. Porosity was quantified visually using a set of six standard samples ranging from 0 to 1.07% porosity by area. The standard sample porosity areas were established using image analysis, a method which was not used for all of the samples as it was extremely time consuming and involved creating further photographic images of each sample. Porosity levels could have been quantified by density measurements, however due to the large volumes of impurity present the theoretical density of each specimen would have had to be calculated. This would have been time consuming and would have introduced errors associated with composition analysis as well as any error present in tabulated density charts.

The results discussed in this paper deal only with the tensile test results however an accompanying paper deals with the results of MLR analysis of the modification and grain size data.

The Effects of Phosphorus

Phosphorus acts as an extremely strong nucleant for silicon phase solidification. This promotes coarsening of the silicon structure so opposing the refining action of the modifiers. This is sometimes regarded as beneficial in hypereutectic alloys where phosphorus is often added to achieve a fine and even dispersion of primary silicon, improving ductility and wear resistance. In the hypoeutectic alloys where refinement of the eutectic silicon is desired phosphorus contamination should be minimised where ever possible. Phosphorus usually enters the aluminium from contact with refractories, tools and crucible glazes, and is often present in virgin alloy at around 4-5ppm and at ever higher levels following subsequent processing. the effect of phosphorus on modification is shown in Figures 1 and 2 (taken from[1C][8]). From these figures an increase in phosphorus level from 5 to 8ppm can be seen to more than double the amount of modifier required to achieve a similar level of modification.

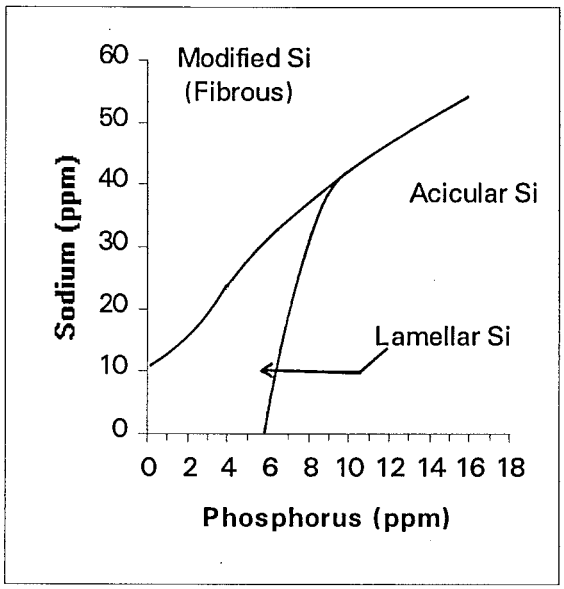

Figure 2: AlSi13 Alloy, solidification time=13sec.

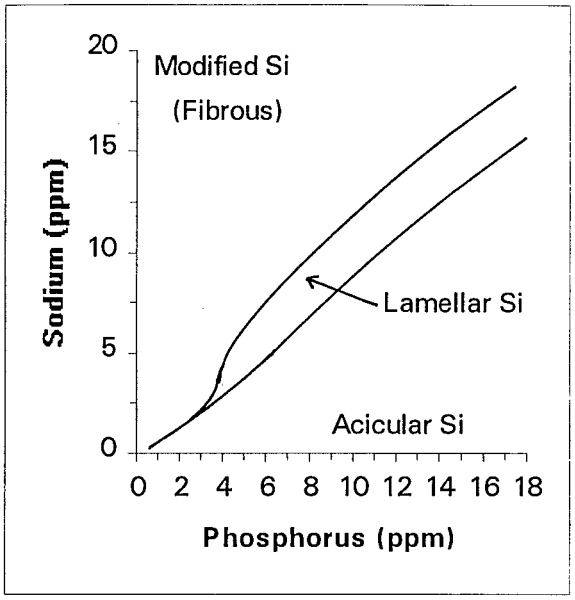

Figure 1: AlSi7Mg alloy, solidification time =13sec.

Colorimetric analysis for phosphorus was attempted by NZAS however achieving the desired accuracy of ±1ppm proved extremely difficult and time consuming. As a result the phosphorus levels present in the samples used in this research remain to be determined. A consequence of this is that it becomes impossible to differentiate between the effects on modification from an individual element and those due to phosphorus its master alloy may also introduce. It is hoped that the phosphorus levels may be established at a later date, so that more information may be gained from the modification and composition data collected.

Results

The following results are based on the outcome of Multi-Linear-Regression (MLR) analysis. The nine MLR outputs from which the following results have been taken are not included due to space considerations. The base tensile properties to which these figures apply may be taken as (9.5%Si no other additional elements); UTS 102MPa, 0.2%PS 75MPa and δL 7.1%.

Silicon

It has been reported that silicon has little effect on tensile properties when varied in the range 4-13%[9]. While preliminary MLR results tended to support this theory definite effects on all three of the measured tensile properties have subsequently been found. Statistically the least significant of these is the trend associated with 0.2% Proof Stress, even so this factor is significant to the .00065% level. As can be seen in figure 3 tensile strengths vary by as much as 14MPa in the range 9.5 to 13.5% Si, with the optimum level appearing to be at 11.3% Si. Although no minimum proof stress is required by the cast Al-Si property standards this property also has an optimum associated silicon level that being ≈12.7%Si. The decrease in ductility associated with increasing levels of silicon is significant but is of a magnitude which can be easily compensated for by correct modification.

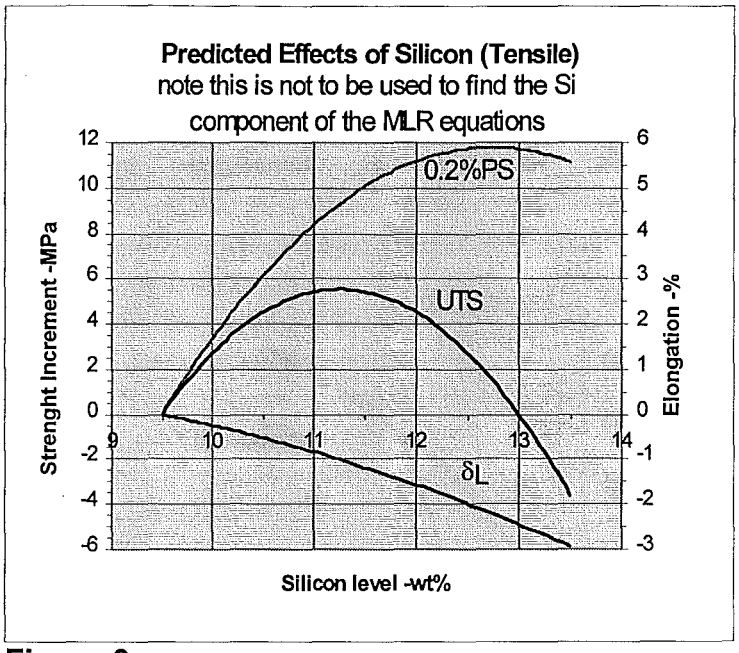

Figure 3

Sodium

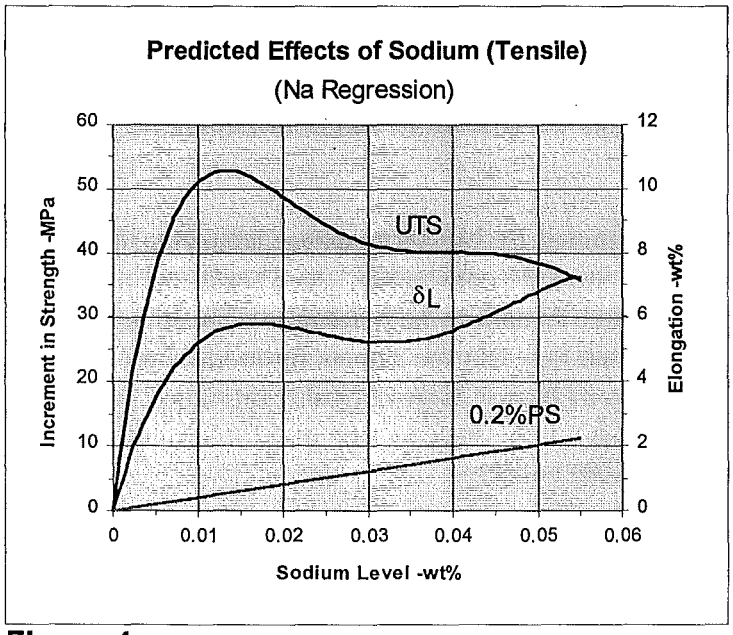

Figure 4

Of all of the elements investigated sodium has by far the greatest effect on the tensile strength and ductility.

The optimum properties are obtained in the region 0.012 to 0.018%Na. By comparing the effects of sodium shown in figure 4 with those of strontium shown in figure 6 it is apparent that even when sodium is added in excess (0.02 to 0.05%) the gains in strength and ductility exceed those possible with strontium, even with the strontium at is optimum level. The gains in strength attainable with sodium are of such high magnitude that correct and consistent addition of this modifier is clearly the most critical step in producing acceptable physical properties. Unfortunately the addition of this element in a consistent manner is extremely difficult.

Strontium

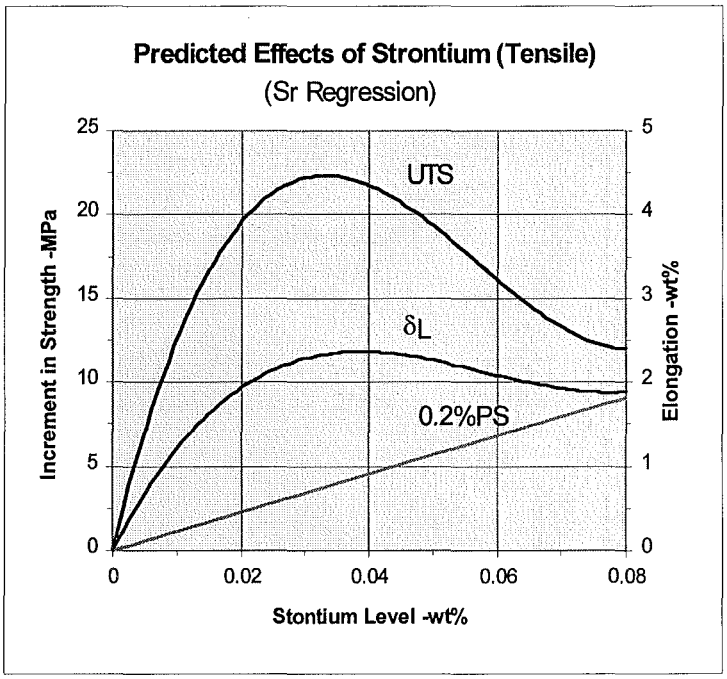

Figure 5

As mentioned above strontium even when added at its optimal level does not cause the same huge gains in strength and ductility associated with sodium. Strontium is widely accepted as being superior to sodium when dealing with AlSi7Mg alloy, this is based on a number of issues the main ones being: the effects of over-modification are not as severe with strontium; strontium is easily added to the ingot prior to purchase so that no subsequent additions need to be made in the foundry; the AlSi7Mg alloy is widely used in permanent mould casing where the differences in strength between Na and Sr modification are far smaller and finally the problems associated with increased gassing when Sr is added have largely been overcome. The results shown in figures 4 and 5 suggest that when dealing with sand cast AlSi eutectic any handling benefits given by Sr are insignificant in comparison to the strength gains possible with Na.

Iron

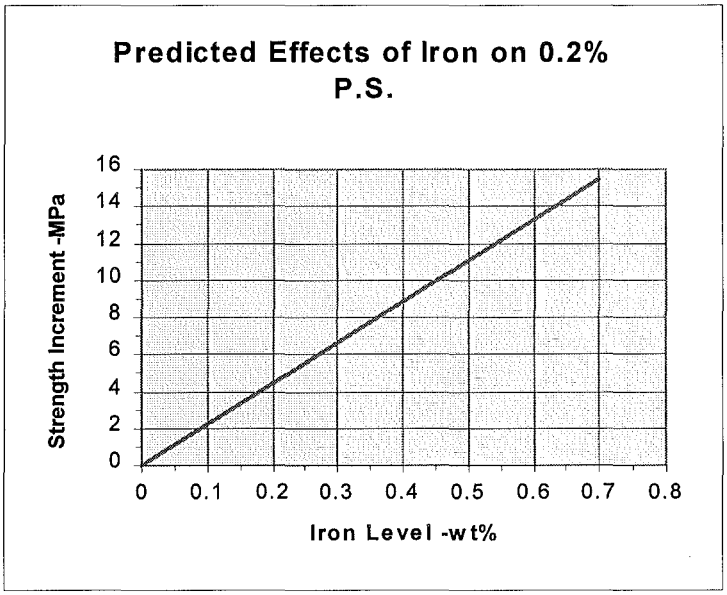

Figure 6

Iron is usually the major impurity present, it is normally found in the range 0.1-0.2% in virgin alloy and at higher levels in secondary product. As mentioned earlier iron is often associated with brittleness and large reductions in ductility especially when present at levels beyond 0.3%. When iron levels exceed 0.3% correctives are often added -most commonly manganese[3]. Adding manganese causes $(FeMn)_3Si_2Al_{15}$ to form which is regarded as less detrimental than plates of $FeSiAl_{15}$ which would otherwise form. Both of these phases were observed in the iron and manganese samples used in this research. By looking at Figure 7 it can be seen that iron correction due to manganese seems only to occur at high levels of both elements (eg beyond 0.4% of each). While the iron does have a strong negative effect on ductility iron levels will not normally vary more than 0.1% during processing. this relates back to a loss of 0.5% in

elongation. Any further efforts to further reduce iron levels at the primary production site should clearly be based on factors such as fatigue resistance and impact strength rather than ductility. It is obvious from figures 6-8 that iron also has a large positive influence on tensile and proof strengths, however the gains in tensile strength are lost when more than 0.3% manganese is added.....exactly the amount needed for iron correction to commence.

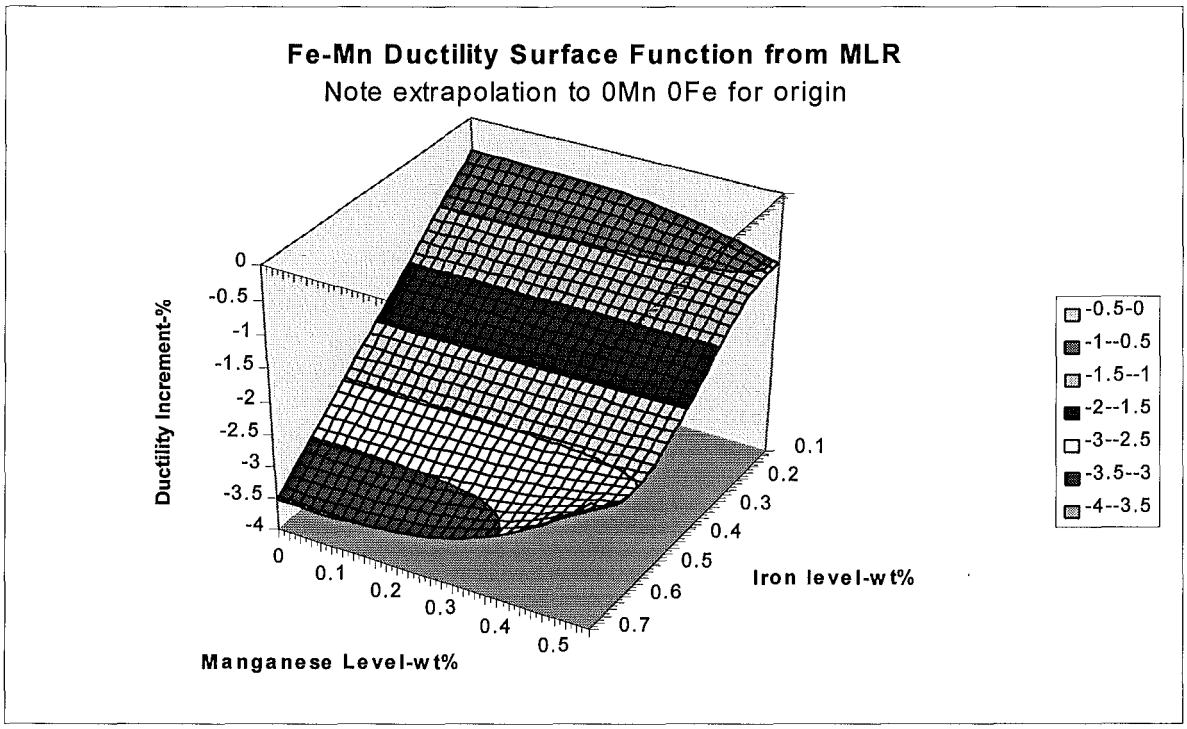

Figure 7

It should be noted that the indicated increase in ductility with high iron and manganese levels was higher with the sodium modified samples than those modified with strontium

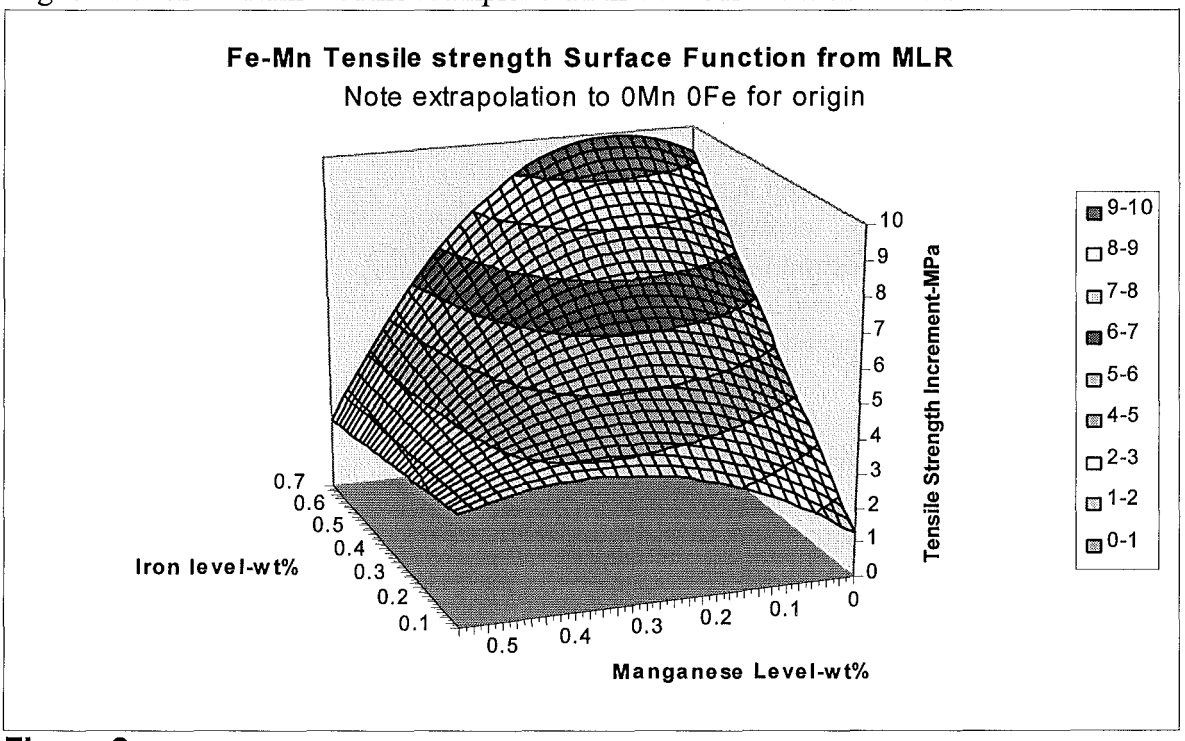

Figure 8

Manganese

The main effects of manganese have been covered in the above iron section, due to the effects of the two elements being strongly interdependent (see figures 6-8). Unfortunately the effect of manganese on the 0.2% proof stress could not be found.

Magnesium

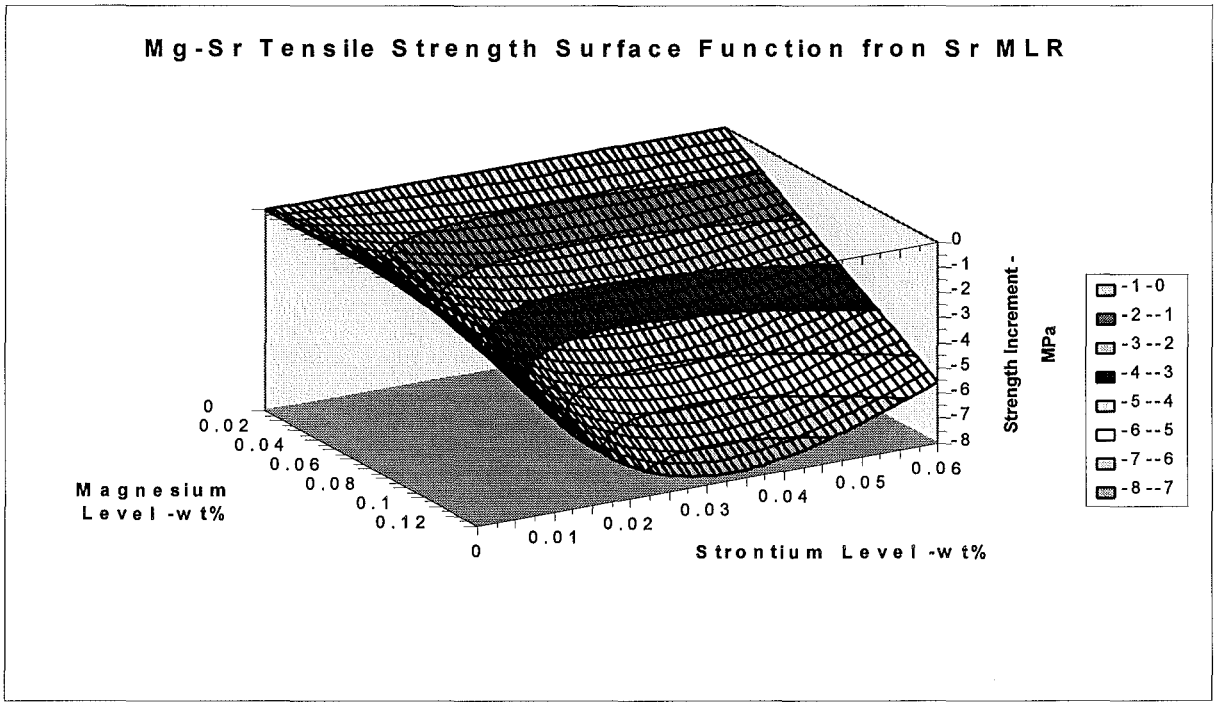

Figure 9

As shown in figures 9-11 magnesium has detrimental effects on strength and ductility which are accompanied by increases in proof strength. The decrease in strength appears to be closely related to the level of modification present, the higher the degree of modification the stronger the influence of magnesium. As no decrease in strength is found when zero modifier is added magnesium would seem to act to reduce silicon refinement but not reduce strength directly. This is supported by MLR results which are presented in an accompanying paper, this paper shows that as the magnesium level increases the amount of modifier required to achieve optimal modification increases significantly. The fact that as the magnesium level rises so does the amount of modifier required to give optimal modification should mean that as the magnesium level rises so

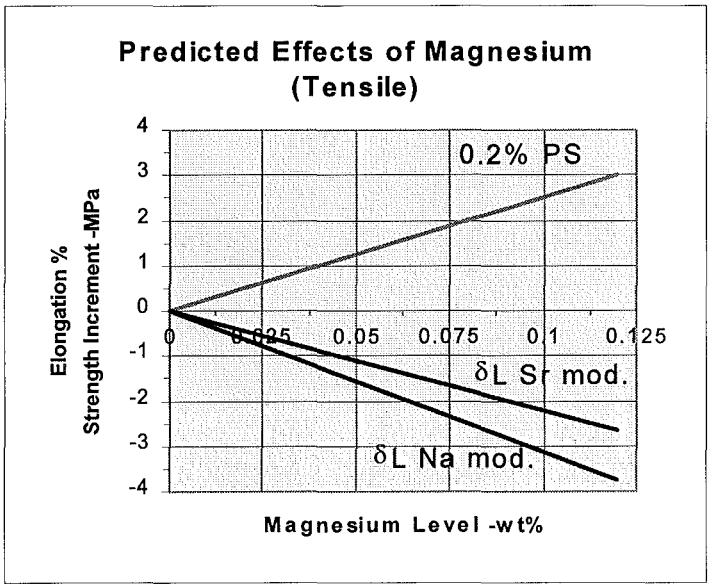

Figure 10

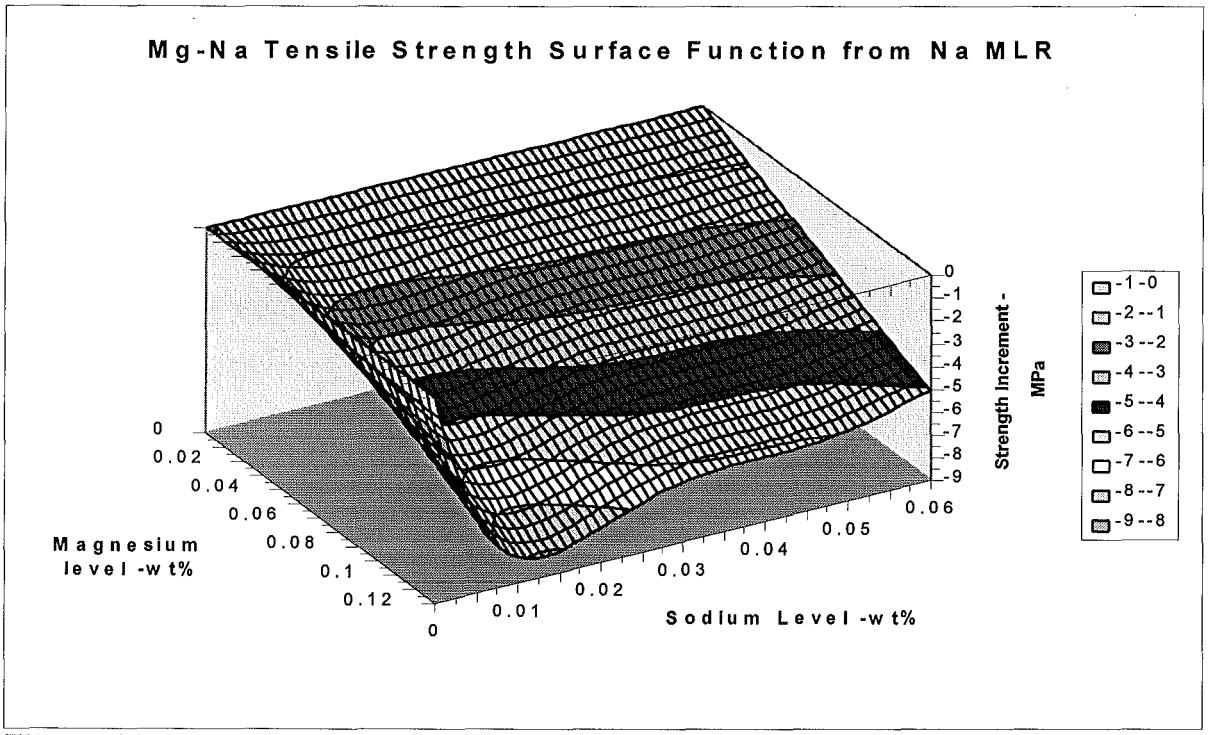

Figure 11

does the strength in the region 0.015-0.03%Na or 0.04-0.05%Sr. This does not appear to be the case as functions incorporating this strength rise have been found to be statistically insignificant. This means that when additional modifier is added to compensate for magnesium the modification rating should be restored but the strength will not improve with this improved modification. If these trends continue at lower silicon and higher magnesium levels sand cast AlSi7Mg alloy should show optimal strength with slight under-modification.

Titanium

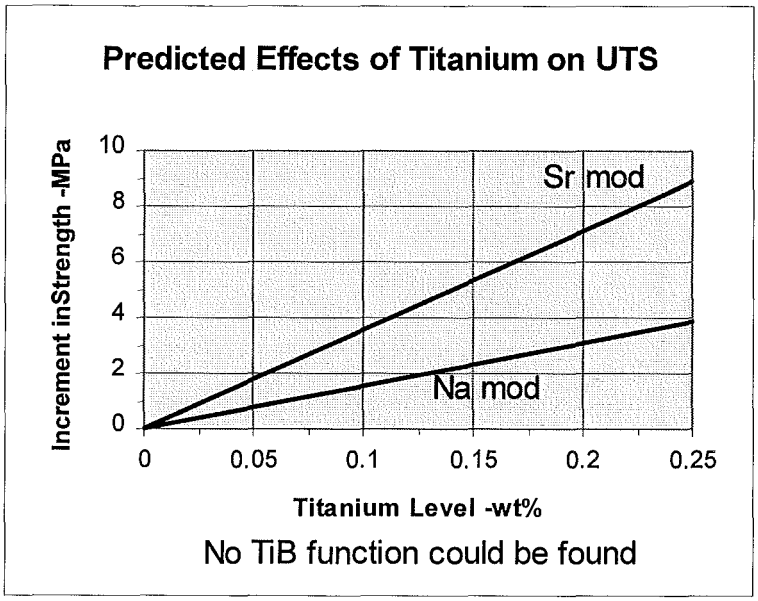

Figure 12

Titanium has long been added to aluminium alloys of all types to provide grain refinement. Grain refinement is important with cast alloys as the soundness of resulting castings is substantially improved, this is more due to finer more even porosity dispersions rather than any actual reduction in the amount of porosity present. Figures 12 and 13 show that the effects of titanium are strongly associated with the boron level as would be expected, however no effect on the 0.2% proof strength could be found. Figure 12 shows that more strengthening due to titanium occurred in the strontium modified samples than those modified with sodium. This

may be a result of the inherent lower strength of the strontium samples or due to the fact that titanium acts as a strong aid to modification particularly in the presence of strontium (see second paper by the same author).

Titanium influences ductility in a slightly negative way except in the presence of boron, at high titanium and boron levels the titanium acts to moderate the strong negative born influence.

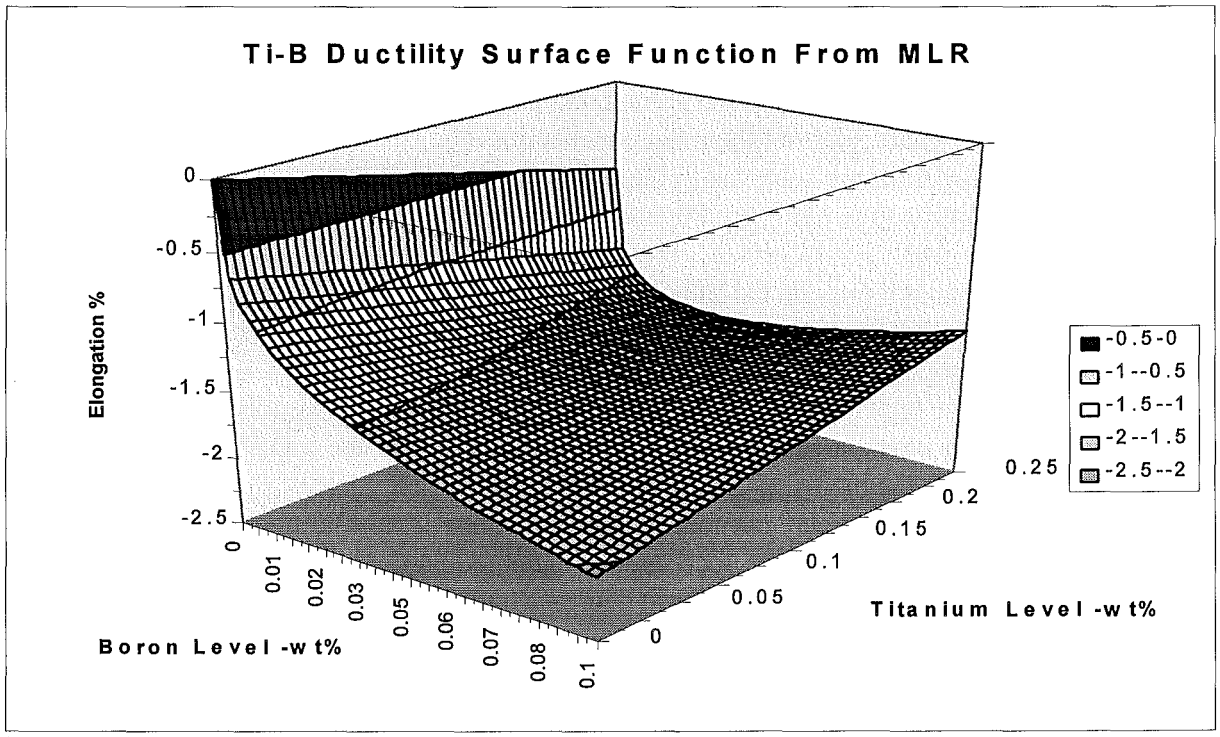

Figure 13

Boron

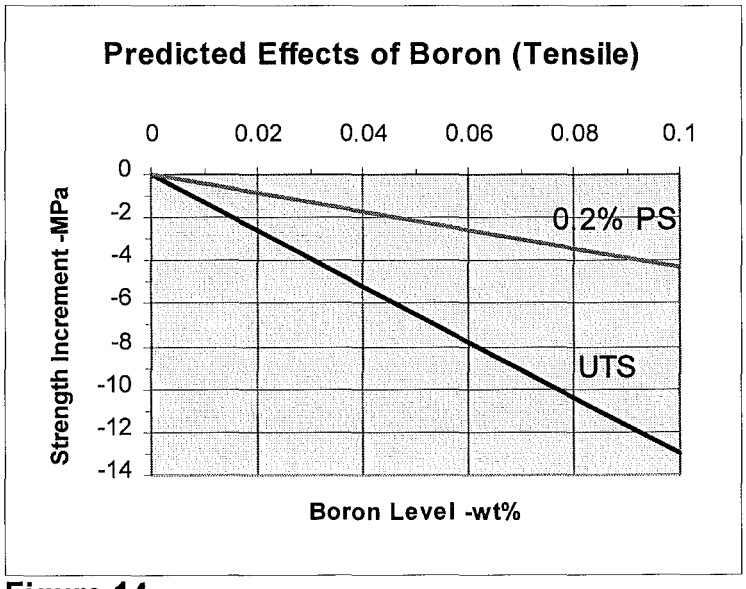

Figure 14

The effect boron has on ductility is shown in figure 13 above. As can be seen the boron is highly detrimental to ductility even when added in amounts as small as 0.02%. Figure 14 also shows that boron is detrimental to strength and proof strength. As the boron was added via two separate master alloys, one unintentionally of the AlB_{12} type, the MLR residuals associated with each form of addition were separated and plotted. From this plot no clear distinction could be made between the addition types, hence it would seem that boron even from commercial TiB grain refiners causes no clear improvement in the tensile properties. Boron is usually added to grain refiners because it promotes finer grain size and reduces fading of the refinement when

prolonged holding times are encountered. Hence the effects of boron may well be far less detrimental when longer holding times are encountered as is usual in commercial foundries. These results would tend to indicate that boron should only be added to the level required to achieve the desired casting soundness.

Conclusion

Although this paper has only dealt with the outcome of investigations into the tensile properties of the AlSi eutectic alloy it has provided some conclusive results to questions which have been the subject of much debate. In brief the main conclusions are.....

-Optimal properties are achieved in the range 11.3-12.5%Si.

-Sodium modification can increase strength and ductility by as much as 54MPa and 6% elongation.

-Strontium can not provide the same gains in strength and ductility as sodium.

-Iron is detrimental to ductility but this is not a major concern given the levels of iron found in most commonly used alloy.

-Correction of high iron levels by the addition of manganese is only of use when the level of each element exceeds 0.4%. When this occurs the gains in tensile strength associated with the increased iron levels may well be totally lost.

-Magnesium is detrimental to modification and consequently strength and ductility.

-Titanium causes significant increases in strength particularly in strontium modified alloy, it is also responsible for a slight decrease in ductility.

-Boron appears to be highly detrimental to all tensile properties so its use must be moderated so as to induce the desired level of grain refinement and hence casting soundness without causing to great a loss of strength and ductility.

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Appendix Q-(v) IPENZ95c

The Influence of Melt Contaminants on the Modification and Grain Refinement of Aluminium-Silicon Eutectic Alloys

W.D. Shilvock[1]

Abstract

Modification and grain refinement are two of the most important melt treatments carried out on molten Aluminium-Silicon alloys. Following the casting and analysis of approximately 500 Aluminium-Silicon test samples detailed Multi-Linear-Regression has been carried out revealing the influence of various impurities upon the silicon morphology and grain size. The quantified effects of elements such as Titanium, Sodium, Strontium, Magnesium etc are provided.

Introduction

The results reported in this paper come from extensive experimental and statistical analysis of 495 sand cast Al-Si eutectic test pieces. The method of sample production is briefly covered in the accompanying paper by the same author. The production method used aimed to reproduce the processing steps and environment encountered in a small commercial foundry. As a result conventional inert gas degassing has been used as have commercially available master alloys. The samples used to generate the data analysed in the following report were all cut from the same position on BS1490 tensile test bars. All 495 specimens had varying composition within the ranges indicated below....

Si	10-13%
Na	0-0.05%
Sr	0-0.07%
Mg	0-0.1%
Mn	0-0.5%
Fe	0-0.6%
B	0-0.05%
Ti	0-0.2%

This set of ranges corresponds to the composition limits permitted in BS1490-LM6, this being one of the most common alloy specifications used in N.Z. when obtaining AlSi eutectic casting alloy. As mentioned in the previous paper, the wide composition limits permissible within the LM6 range mean that it is one of the easiest composition standards to meet with secondary metal. Unfortunately meeting the physical requirements of the British Standard on a consistent basis is virtually impossible unless initial metal compositions are very closely controlled.

Prior to casting LM6 usually goes through several processing steps, two of these which are sensitive to composition variation are the addition of grain refining and modifying elements. The control of these two steps is crucial if optimal physical properties are to be achieved.

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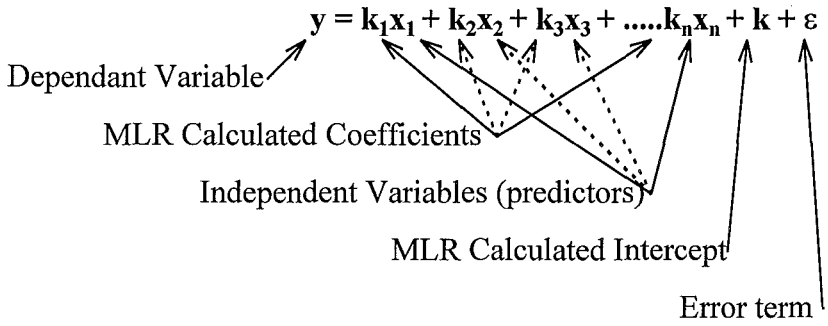
MLR -What is it?

Multi-Linear-Regression (MLR) is a statistical method used to assess the explanatory value of many different plausible predictors in the explanation of variance in a dependant variable. MLR is basically a least squares fit method with several variables which may be input in a linear or non-linear form. The result of an MLR analysis is a set of predictors (or independent variables) which may be used to assess the influence of various factors on the monitored dependant variable. An example of the general equation that MLR solves is shown below.



The MLR analysis calculates the constant values (k's) in the above expression and also indicates both the predictive worth of the overall equation and the worth of each individual independent variable. If all or almost all of the relevant factors controlling the variance of the dependant variable are included in the regression as independent variables the resulting MLR equation should have a predictive error no higher than the error due to measuring the input variables. If on the other hand influential factors are not included in the MLR then the predictive worth of the overall equation will be low. However if the significance of some of the variables is statistically high their coefficients and hence influence may be quantified. The ability of an MLR equation to predict an outcome is displayed in the form of an R^2 value. This value may be interpreted as the percent reduction in error present compared with a simple mean value approximation.

Grain Refinement

What Constitutes a Grain?

The practice of chemically grain refining cast aluminium alloys has been widespread for a number of years yet surprisingly little data exists indicating the influence of alloy composition upon the level of grain refiner required or the degree of refinement which may be achieved. This lack of data is compounded by the complexity of defining exactly what constitutes a grain in the LM6 structure. With alloys containing predominantly primary aluminium a "grain" is conventionally regarded as the region occupied by aluminium of a single orientation stemming from the growth of a specific aluminium dendrite. When alloy of composition approaching a eutectic is encountered this definition becomes inappropriate due to the large proportion of mixed eutectic phase, with hypereutectic alloys the definition losses all significance as no primary aluminium exists. In the case of hypereutectic Al-Si the primary silicon solidifies as faceted unconnected blocks in a matrix of eutectic colonies. Within the LM6 range the silicon can only represent a very minor proportion of the structure so the hypereutectic alloy properties are governed mainly by the form of the eutectic.

The issue of eutectic solidification has been extensively studied by several authors and is dealt with in papers by Abott et all[1], Ohno et all[2] and Kobayashi et all[3]. In general when a eutectic forms it does so in a manner very similar to that of a single phase, eg dendrites which grow into equiaxed or columnar colonies. These colonies nucleate from primary silicon particles and grow in a radial manner away from the nucleus. an example of a equiaxed eutectic colony is shown in figure 2d.

In this study a grain has been defined as the region occupied by primary aluminium of a single orientation or the region occupied by a single eutectic colony.

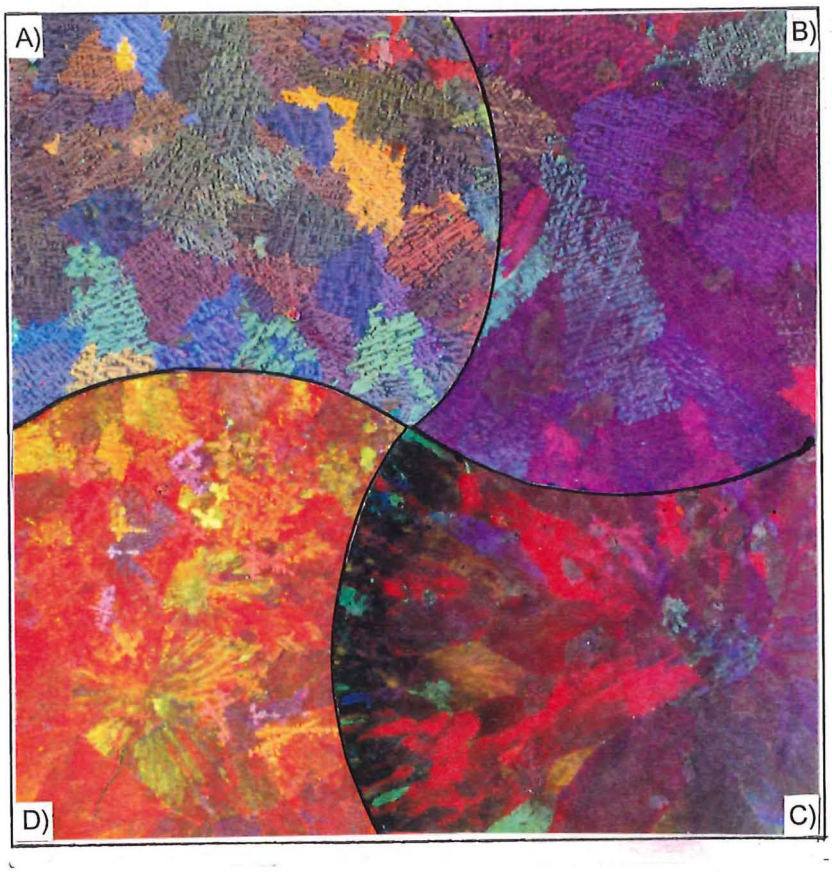
Why Grain-Refine?

Grain refinement of cast aluminium alloys is carried out to improve casting soundness. The finer grain structure also more evenly disperses any impurity which collects ahead of the solidification front. The addition of grain refiners such as titanium and boron does not reduce the amount of porosity present but it causes a finer dispersion of voids which results in less casting rejects due to gross porosity and localised loss of mechanical integrity and pressure tightness. MLR (Multi-Linear-Regression) results from analysis carried out in the course of this research have indicated that boron is in fact the source of some porosity, this however may not be the case when longer melt holding times are encountered as would be the case in a commercial foundry.

Quantifying the Grain Size

Revealing the grainsize of the alloy in question is achieved by projecting light of varying colour and angle onto a macro-etched sample. this highlights the aluminium in various colours depending on its orientation. Figure 1 illustrates the degree of grain refinement which can be achieved by the addition of Ti and B as well as the changes due to other factors such as silicon and modifier variation.

The grain size of cast aluminium alloys may be quantified in a number of ways, for this research photomacrographs such as those shown in figure 1 have been compared to ASTM grain size plates. The ASTM plates provide a set of reference grain sizes which may be easily converted to alternate units such as grains per mm^2. In general the lower the macro grain number the courser the grain size. It should be noted that the ASTM scale is not linear and grain size 2 is not twice the size of grain size 4. Quantifying the grain size in this manner can cause some problems as figure 2 illustrates. Figure 2a shows an unrefined equiaxed sample which may be easily compared to the ASTM standards. Figure 2b shows a sample displaying distinctly columnar grains, very few samples showed this problem but those that did were analysed by the Jeffries (planimetric) method. A sample which is virtually 100% eutectic and displays columnar colonies is shown in figure 2c (most colonies tended to display a columnar structure), this sample is in fact an example of the worst case of this type encountered it was also analysed by the Jeffries method. Finally figure 2d shows an equiaxed eutectic colony where the colony has grown out from a primary silicon particle. This type of growth was only found in the unmodified regions of the samples containing in excess of 13% silicon. This is exactly what was expected with the leading phase of the eutectic providing a primary nucleus from which the eutectic growth could occur.



With two of the samples revealing the grain boundaries proved virtually impossible as a result they were discarded from the statistical analysis.

Figure 2: Various Grain Sizes and Types Present in AlSi Eutectic Alloy (x4.4)

Grain Size Results

The below MLR results relate ASTM Macro Grain Size Number to sample composition. The composition variables were established using OES analysis at NZAS, they are in units of weight percent. Of the 21 elements monitored only those mentioned above as well as copper were included in the regression process as these were the only elements to show composition variances of significant order.

Overall Grain Size Equation

$$\text{ASTM G(M)} = 32.1848 .B^{0.5} - 67.4788 .(Ti.B)^{0.45} + 19.7787 .Ti - 0.0420(Si^2 - 26.09.Si)$$
$$- 0.7836.Mn + 17.3521.Na - 6.92630.Sr + 0.3257$$
$$R^2=0.743$$

The independent variables above are listed in order of statistical significance with the boron term of significance to the 4E-114% level and the strontium to the 4% level (t test two tailed). It can be seen that the above model does not vary between the types of modification used. Variations in the influence of boron and manganese dependant on the modifier used were encountered but the boron variation was minor and the apparent variation with manganese was difficult to substantiate as statistical significance of the strontium manganese effect was relatively low.

Titanium and Boron

It may be expected that titanium and boron would act in a synergistic manner, in this instance that does not seem to be the case. As shown in figure 3 boron acts as a far stronger grain refiner than titanium. At low titanium levels (below 0.08%) grain refinement is greatly improved by the addition of boron however the presence of titanium at these levels seems only to hinder the action of the boron alone. At higher titanium levels the refining action of the titanium dominates and the addition of as little as 0.01% boron reduces the refinement to levels similar to that achieved with 0.08% titanium alone.

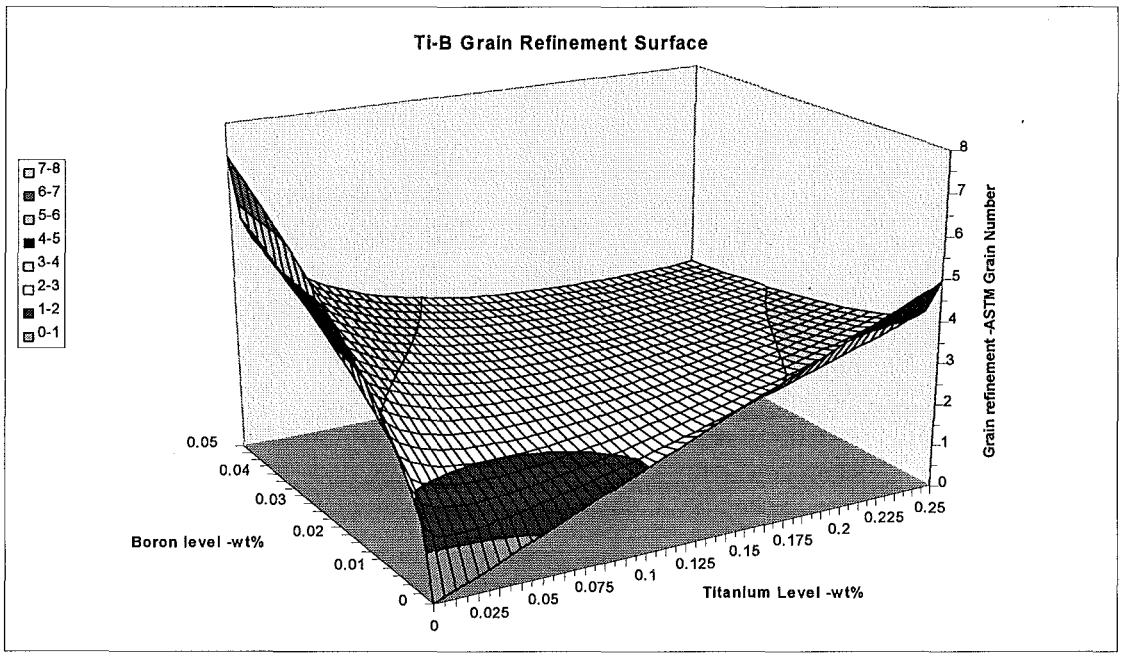


Figure 3: Predicted Grain Refinement Due to Ti & B

Sodium and Strontium

As can be seen in figure 4 the modifiers have a minor effect upon the grain size, this is even more evident when you realise that they are usually present in levels no higher than 0.03%. Initially it was assumed that both modifiers would have either a positive or negative effect but as shown sodium tends to refine the grain and cell size while strontium coarsens it. Of the two terms lower statistical significance is associated with the strontium even so this term is significant to the 4% level.

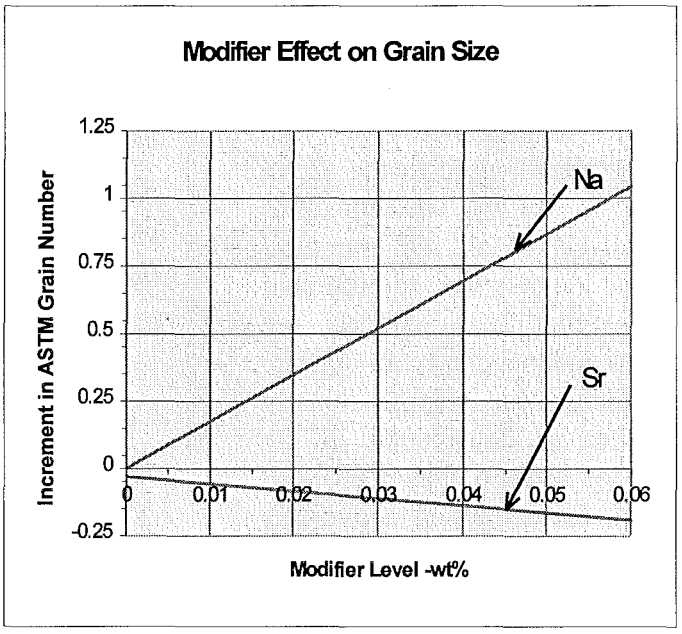


Figure 4: Predicted Grain Refinement Due to Na & Sr

The sodium factor included in the above MLR equation came from analysing all 495 samples, when only the sodium samples are analysed the factor increases slightly to 20.14 which is what is displayed in figure 4. This difference amounts to less than 0.05 G (M) ASTM units which is an amount smaller than could reasonably be measured. The strontium factor was consistent to within 0.3% whether all of the samples were analysed or simply those containing strontium.

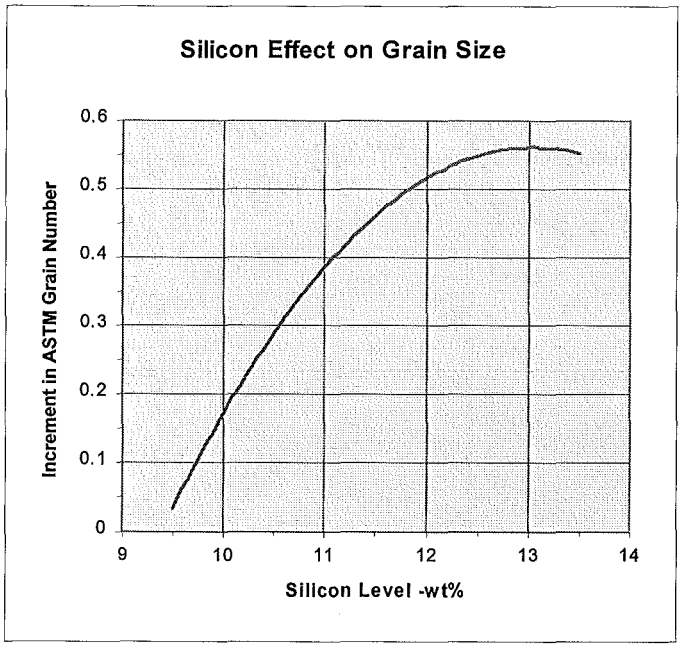


Figure 5: Predicted Grain Refinement Due to Si.

Silicon

Apart from the traditional grain refiners the element which has the greatest effect on grain size is silicon. As is clear in figure 5 the largest refinement in grain size is associated with 12.5-13.5% Si which corresponds to the point at which primary aluminium dendrites cease to be observed and eutectic cells begin to increase in size

Manganese

No influence of either iron or magnesium could be detected however manganese was detected as being a detrimental impurity. The statistical significance of the manganese factor used in the above equation is 0.17% which comes from analysis of all 493 samples. When the models for sodium and strontium modified samples are looked at independently it appears that the manganese is approximately three times as detrimental in the presence of sodium than it is with strontium, as mentioned above this is difficult to substantiate statistically.

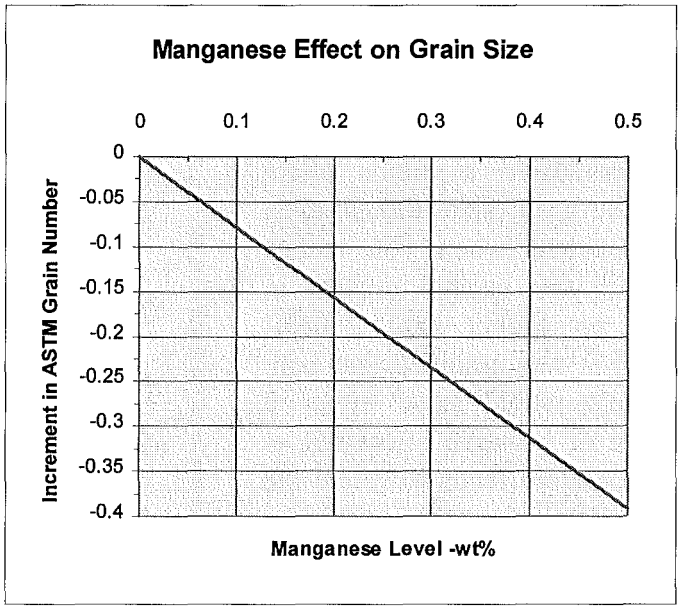


Figure 6: Predicted Grain Refinement Due to Mn.

Modification

The structural modification of cast AlSi alloys is achieved through the addition of minor amounts of sodium or strontium. Even though modification is possibly the single most crucial step in the casting process the interaction of other elements with this silicon refinement process is poorly understood. Several studies have been carried out to investigate the interactions of various modifiers (this is covered by Gruzleski[4a]), but virtually no data exists regarding the effects of common impurities such as iron, titanium, manganese and magnesium. It is well established that sodium and strontium are compatible as modifiers, similarly it is known that phosphorus and antimony reduce or eliminate the refinement these elements cause. While N.Z. foundries tend to use either sodium or strontium modification the bulk of the foundry alloy becoming available for recycling is from imported components such as automotive wheels. Hence it is feasible that appreciable levels of mixed modifiers and refiners such as sulphur and antimony may enter the domestic alloy cycle.

Modification is an extremely complex issue which is influenced by issues such as solidification rate, the holding time prior to casting, the form in which the modifier is added and at what temperature modification took place. In this study sodium was added as elemental sodium and strontium was added as a 10% strontium master alloy. Modification took place at approximately 730°C and casting at around 710-720°C. Cooling was controlled by the sand moulds which were made using a air setting resin bonded sand.

Four typical modification microstructures are displayed in the three figures below. It can be seen that sodium promotes a finer structure than strontium it also does so at lower addition levels. Much published data exists on the transition from the coarse to the modified state, but not a great deal on the partially modified transition which is often highly heterogeneous, sometimes in a banded form and sometimes as cells, Clapham and Smith[5] have studied this in some detail.

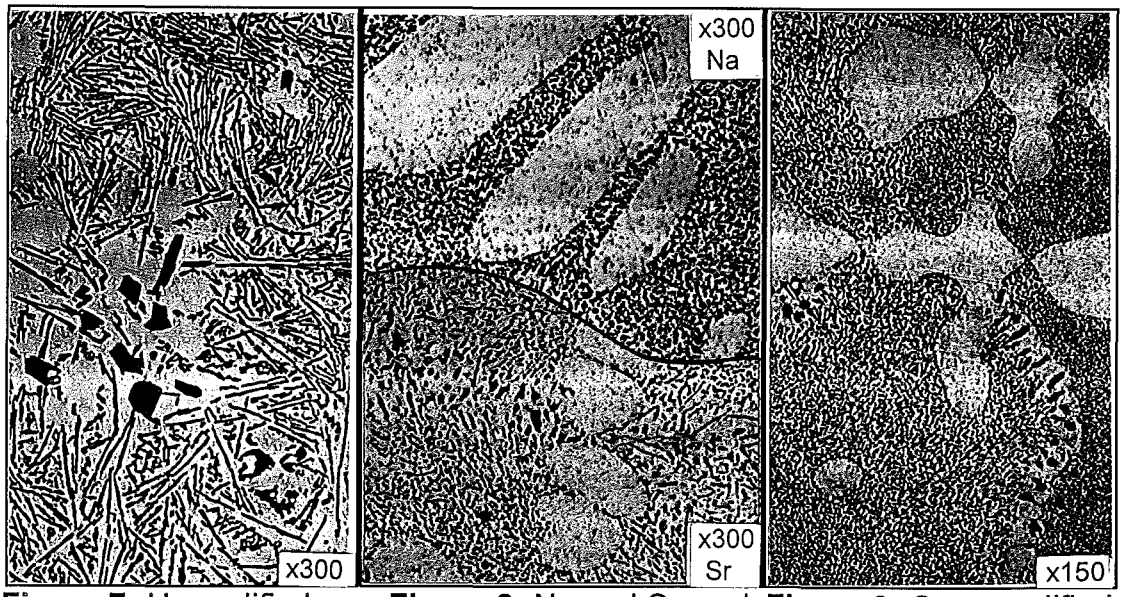


Figure 7: Unmodified **Figure 8:** Na and Sr mod. **Figure 9:** Over modified

Quantifying Modification Level

As mentioned above eutectic modification is often not homogeneous even on a microscopic level consequently quantifying the degree of refinement must take into account the amount of each modification state present. In this study the modification rating for each sample was established using standard AFS(American Foundrymen's Society) modification scales[6], and multiplying each scale value by the proportion of the sample area which it represented[4B]. For example if 20% of a samples area is rated 2, 65% rated 3 and 15% rated 4, then the modification rating is...

$$(0.2\times2)+(0.65\times3)+(0.15\times4)=\underline{2.95}$$

One problem which was encountered when using the AFS scale of refinement was that it stops at a refinement level of six which corresponds to an ultra fine fibrous structure, this left the question of what to do with overmodified structures. Two options existed one was to rate the overmodified structure the same as an undermodified structure displaying a similar degree of coarseness (but different silicon shape), the alternative was to set up further standards relating to overmodified and grossly overmodified structures. Each of these options has problems associated with it however to allow clear distinction between over and under modification in MLR predictions it was chosen to use the latter system with additional scales of 7 and 8. At the coarse end of the standard an additional scale of zero was also established so as to help rate the very coarse acicular structure encountered in some high silicon unmodified structures, it is doubtful that this scale would ever be required in alloys of lower silicon level.

Modification Results

The MLR results below relate the sample composition to the AFS modification rating as defined above. The 495 samples monitored have been separated into two groups and regressed dependant upon the major modifier used. Copper has been excluded from the regression equations even though it was found to be a highly significant variable in each set. This was done as the removal of copper from each set of all significant variables yielded virtually no loss in the predictive worth of the final MLR equation. The exclusion of copper increased the significance of both the iron and titanium terms yet no direct correlation between these elements could be found. It should be noted that the copper terms which were established were incompatible and difficult to explain. A regression of the full set of data was carried out in the hope of establishing the interaction of the sodium and strontium, this has been achieved but is not included here.

Overall Modification Equations

Sodium Samples

$$\text{AFS Modification \#} = 83{,}833{,}388\ .(\text{Na Spline}) - 152{,}876{,}158\ .\text{Mg}\ .(\text{Na Spline}) + 2.8315\ .\text{Ti} + 0.965262\ .\text{Fe} + 0.348226$$

$$R^2 = 0.906$$

$$\text{Na Spline} = \text{Na}^5 - 0.17306\ .\text{Na}^4 + 0.011192\ .\text{Na}^3 - 0.0003593\ .\text{Na}^2 + 7.0776\text{E-}6\ .\text{Na}$$

As can be seen below a Si-B term was found for the strontium samples, a similar term of statistical significance could not be found for the above sodium regression.

Strontium Samples

$$\text{AFS Modification \#} = -731{,}626.59.(\text{Sr Spline}) + 1{,}883{,}812.2.\text{Mg}.(\text{Sr Spline}) - .27922.\text{Si}.\text{B}^{0.3} + 3.8796.\text{Ti} + 160.983.\text{Na} - 0.40417.\text{Fe} + 1.227111$$

$$R^2 = 0.7044$$

$$\text{Sr Spline} = \text{Sr}^4 - 0.20533.\text{Sr}^3 + 0.01432.\text{Sr}^2 - 0.0004062.\text{Sr}$$

As with the grain size equations the independent variables are listed in order of statistical significance. The strontium equation iron term is significant to the 4% level, while the sodium equation iron term is significant to the 0.001% level.

It should be noted that the AFS modification number of six represents a very fine "super modification" state. As very few samples displayed this degree of refinement, the MLR predictive rating of 6 can be assumed to be made up of a very well modified structure with some regions of over-modification. Optimal refinement can be assumed to be predicted with a rating of 5.

Sodium (and Magnesium)

The 3D diagram below illustrates the modifying effects of sodium and the interaction magnesium has upon this eutectic refinement. Optimal modification in the absence of magnesium occurs at around 0.15%Na which is in close agreement with the sodium requirement for optimal physical properties as mentioned in the accompanying paper. When magnesium is added it is predicted that maintaining a similar level of eutectic refinement requires increased sodium levels. For optimal modification the predicted sodium requirement rises by as much as 66%, for example 0.025%Na is required when the magnesium level reaches 0.12%. Further investigation of this issue would be interesting as the additional modifier in the presence of magnesium does not appear to translate to improvements in strength. One possible explanation for this could be that magnesium promotes a less homogeneous modification state within the sample, to date this has not been investigated.

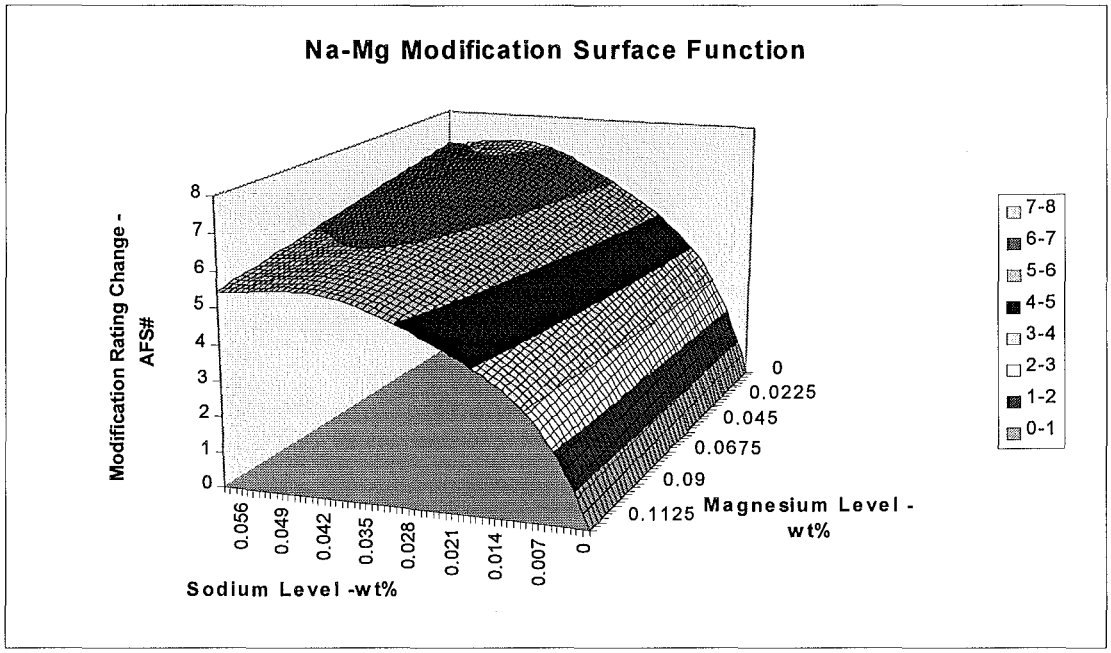


Figure 10:

Strontium (and Magnesium)

When looking at Figure 11, which shows the modification effects of strontium and magnesium, it should be noted that the strontium model has a higher base (or intercept) modification level than the similar sodium model. The variation in base values can be partially explained by the variation in the iron terms and possible heteroscedasticity around the zero axis of the strontium set of data.

Optimal physical properties have been experienced with 0.028-0.035%Sr, in figure 11 this corresponds to a modification rating of approximately 4. Strontium does not cause as fine a eutectic refinement as sodium, it also causes a far less uniformly modified structure, consequently over-modification is not as pronounced and ratings beyond 4 almost certainly indicate very excessive levels of modifier. As shown below optimal modification appears to be available over the range 0.02-0.05%Sr, unfortunately this wide range for optimal modification rating does not correspond to a wide composition for optimal physical properties. A result of this is that accurately detecting the optimal physical state via microscopy could be extremely difficult.

Magnesium displays similar properties in the strontium samples as it does in the sodium set, it coarsens the structure by hindering the action of the modifying element. Even though sodium promotes a finer eutectic the detrimental effects of magnesium are more pronounced in the strontium containing samples than those refined with sodium (typically the magnesium effect is around 44% stronger with strontium than sodium).

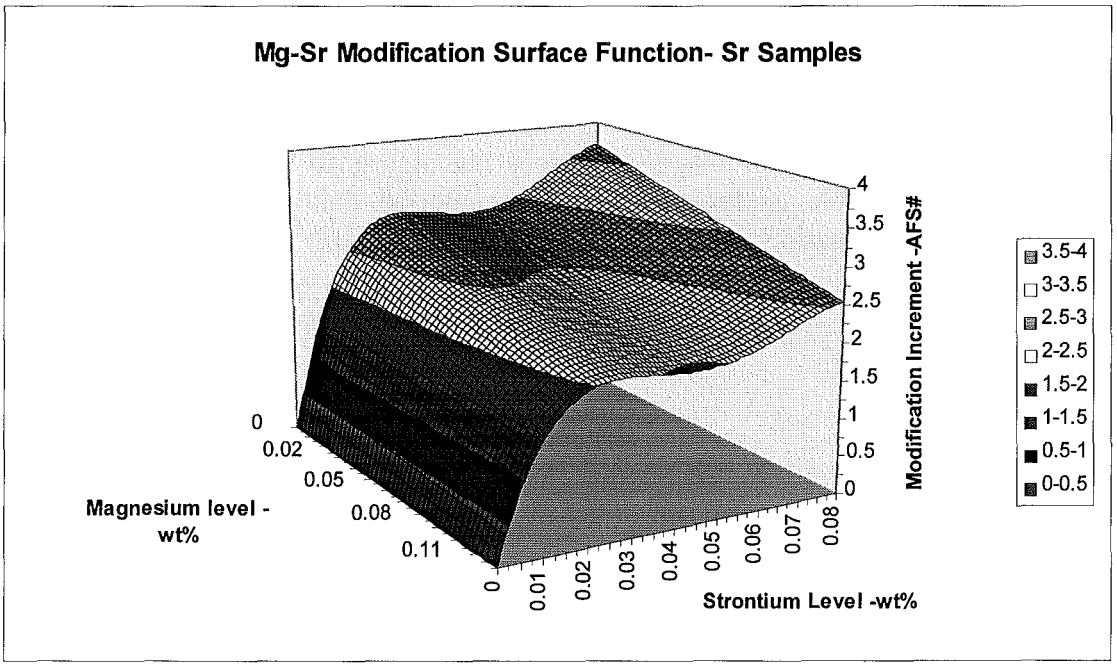


Figure 11:

Silicon and Boron

The strontium regression contains a highly significant term relating the boron and silicon levels to modification, a similar term was not found for the sodium set. The lack of a Si-B term in the Na set is not unexpected as very few samples containing high levels of boron were sodium modified. As shown in figure 12 the addition of boron is highly detrimental to strontium modification, a situation which gets worse as the silicon level increases. It is clear

that even very minor levels of boron can have significant negative effects on the modification level achieved, this is in agreement with the boron ductility function which appears in the accompanying paper.

Titanium

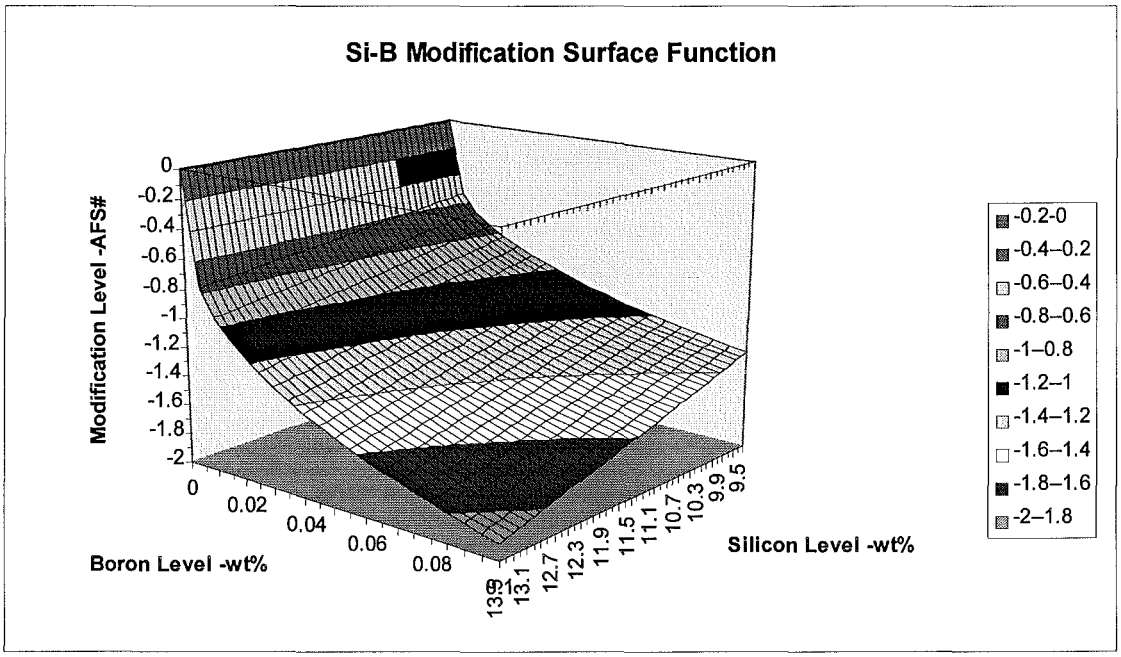


Figure 12:

Titanium has proven to be beneficial to silicon refinement. This modification effect appears to be independent of the level of modifier present or the addition of boron. Sigworth[7] states that "successful modifying elements must be able to combine with phosphorus but not with aluminium", titanium does not meet either of these requirements. Sigworth also goes on to mention a publication which indicates that titanium has no effect on modification of AlSi7Mg alloy, however this observation may be partially explained by the fact that the titanium was added in conjunction with boron. The results illustrated below clearly show that titanium does refine the eutectic, of the two titanium terms found the one with lower statistical significance is still significant to the 1.5E-6% level, hence this trend is indisputable. As can be seen the results indicate that titanium is a more powerful refiner in the coarser strontium structure than the finer sodium equivalent.

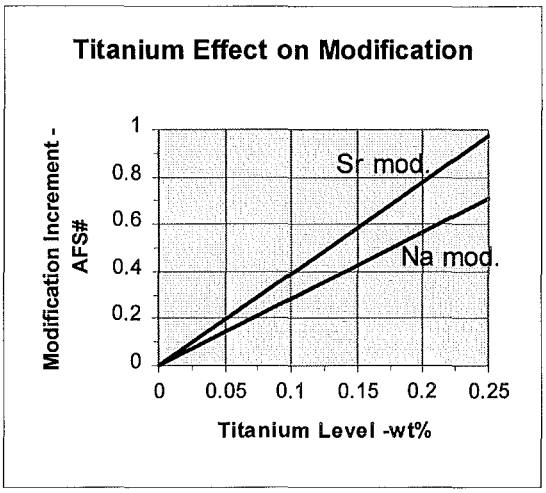


Figure 13:

Several functions incorporating boron were included in the MLR process so as to establish whether the titanium was removing the detrimental effects of boron via the formation of titanium borides or if it was acting independently. No TiB function of significance approaching that of Ti alone could be found, hence the indication is that the titanium action is independent of boron or any other element.

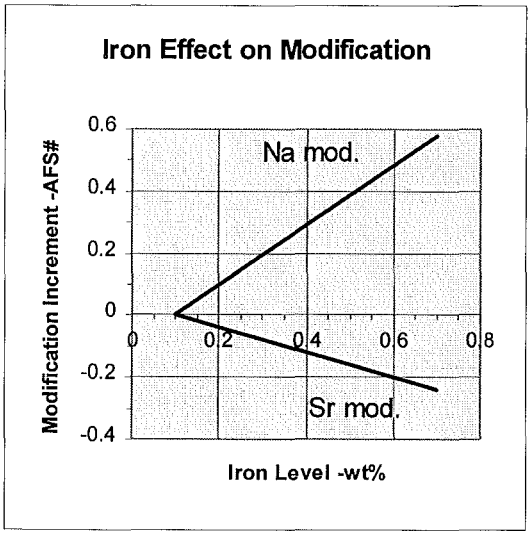


Figure 14:

Iron

The sodium modified samples displayed a very significant (0.001%) beneficial modification effect due to iron, this was not repeated with the strontium samples, in this case the iron term implies that iron is detrimental to eutectic refinement. While the strontium iron term is only significant to the 4% level this should be high enough to conclusively establish whether the iron term is positive or negative. This leads to the conclusion that iron does in fact appear to act in opposite ways dependant on the type of modifier used

Manganese

Manganese levels have not shown any influence on the modification results.

Conclusion

From the analysis carried out to date the following brief conclusions can be drawn....

-Titanium and boron are both powerful grain refiners and they do not act in a synergistic manner. Boron is the more potent of the two and when titanium levels are below 0.08% addition of minor levels of boron greatly improves the degree of refinement. At conventional titanium levels (below 0.08%) the addition of just boron causes more refinement than the addition of the same amount of boron with titanium.

-Silicon content has a major influence on grain refinement with finer grain sizes being encountered in the region 12.5-13.5%Si (the actual eutectic region).

-Sodium provides positive grain refinement while strontium has a minimal negative effect.

-Manganese appears to be detrimental to grain refinement, more so in the presence of sodium.

-Magnesium and iron play little or no role in the grain refinement process.

-Optimal modification with sodium is well defined as is the onset of over-modification. this is not the case with strontium making microscopic detection of the optimal physical state difficult.

-Modification by the conventional elements (Na & Sr) is hindered by the presence of magnesium, more so when strontium modification is employed.

-Titanium acts as a mild modifier, independent of the level of boron or conventional modifier present. this modification effect is more pronounced if strontium is used than it is with sodium.

-Boron is detrimental to modification even when it is added in very minor amounts. this coarsening effect becomes worse as the silicon level increases.

The modification and grain refinement results discussed above are in agreement with the physical property results covered in an accompanying paper.

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Acknowledgments

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